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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Arc Spectra of Yttrium, Erbium, and their Intermediate Fractions. JOSEF MARIA EDER (*Chem. Zentr.*, 1916, ii, 455—456; from *Sitzungsber. K. Akad. Wiss. Wien. Mathem. naturw. Kl.*, [11 *A*], **125**).—The author has redetermined the spectrum of yttrium, using a very pure specimen of yttrium sulphate; the measurements cover the weaker γ-lines from λ 7881—2231. The emission spectrum of yttrium in the electric flame arc is a mixture of three spectra—a well-defined, strong line spectrum and two types of band spectra. The most characteristic form of the latter consists of groups of regular bands the heads of which are rough and shaded towards the red; these are resolved at great dispersion into a system of groups of very fine lines. In addition to these bands, there is also a weak band spectrum composed of indistinct lines, which only appears after protracted illumination, and in consequence of its indistinctness could not be measured.

The yttrium line spectrum between λ 7881 and 2231 contains 706 lines, the wave-lengths of which are given in tables. The yttrium sulphate was free from erbium and thulium, but contained traces of aldebaranium and holmium. In the band spectrum of yttrium, the first group (α) extends from λ 6338—6132, the second (β) from λ 6137—5972; the third group (γ) is less defined, the most marked band head occurring at λ 5956. The groups of bands of shorter wave-length are weaker and less definite, and their structure is less regular than that of the α-, β-, and γ-groups. In the region λ 6338—5838, the author finds 20 lines of the yttrium line spectrum and about 700 line components of the yttrium band spectrum.

The arc spectrum of erbium in the region λ 6880—4471 has been measured afresh; the author finds 1780 lines against 800 previously recorded. The results obtained with different preparations of erbium are so discordant that it appears doubtful if the specimens obtained up to the present are sufficiently uniform. The investigation of erbium preparations from the fractions lying towards the thulium groups shows them to contain in all probability the new element dubhium, in addition to thulium and denebium; only minute amounts of yttrium are present. In the arc spectrum of erbium fractions closely related to yttrium, all the brighter yttrium lines are present accompanied by very large numbers of erbium lines, whilst the lines of the thulium group are not so marked. An erbium fraction containing much yttrium yielded a line spectrum in the electric arc between carbon poles in which 4045 lines were measured between λ 6492 and 2326. In addition to a number of holmium lines, this spectrum contained many unidentifiable lines, which point to the presence of a new element (erbium III). The spectroscopic investigation of erbium preparations containing yttrium gave indications of a fission of holmium.

H. W.

The Quantitative Absorption of Light by Simple Inorganic Substances. I. The Haloids of the Alkali Metals and Hydrogen. PETER JOSEPH BRANNIGAN and ALEXANDER KILLEN MACBETH (T., 1916, **109**, 1277—1286).—The curves obtained by plotting the molecular extinction coefficient against the frequency of the incident light show that the haloids of hydrogen and the alkali metals are not diactinic, but exhibit well-marked selective absorption. For a given halogen, the position of the band is independent of the electropositive element or group, the selective frequencies for the chlorides, bromides, and iodides being $1/\lambda = 3730$, 3570, and 2803 respectively. The frequency thus decreases as the atomic weight of the halogen increases.

The curves for the chlorides and iodides show that the extinction coefficient increases with increase in the atomic weight of the positive radicle, but lithium is an exception to this rule.

In seeking for an explanation of the selective effects, chlorine gas was examined, and found to exhibit strong absorption with a minimum at $1/\lambda = 3060$. Halogen-substituted organic compounds give only slight general absorption. These results seemed to show that the selective effects are due to the halogen ions. Since, however, the molecular extinction of the alkali haloids increases with increasing concentration of the solution, it would appear that the bands are not due to the free ions themselves, but are the result of vibrations set up in them under the influence of the positive ion.

The fluorides examined showed no selective absorption, and it is suggested that the characteristic frequency lies outside the range of ultra-violet rays examined. H. M. D.

The Influence of Solvents, etc., on the Rotation of Optically Active Compounds. XXI. The Relationship of the Rotatory Powers of Ethyl Tartrate, *iso*Butyl Tartrate, and *iso*Butyl Diacetyltartrate. THOMAS STEWART PATTERSON (T., 1916, **109**, 1139—1175).—In continuation of previous work (T., 1913, **103**, 145), which was considered to show that in the temperature–rotation curves of ethyl tartrate beyond the maximum actually demonstrated there should be a minimum rotation of positive, but not high value, the rotations of homogeneous ethyl tartrate, homogeneous *iso*butyl tartrate, and homogeneous *iso*butyl diacetyltartrate, and of these esters in solution in a number of solvents, have been examined for light of six or more colours. Salicylaldehyde, benzaldehyde, pyridine, and quinoline tend to displace the maximum rotation in ethyl tartrate towards a lower temperature and a higher rotation value in the sequence given, the first-mentioned solvent being least powerful. In the last three solvents the curves are obviously tending towards minimum values at high temperatures, this minimum being actually reached in the case of quinoline. It might perhaps be that, since the curves for different colours of light in the case of ethyl tartrate intersect before the maximum, they ought again to intersect after the maximum is passed and before the minimum is reached, in which case a region of visibly anomalous rotation–dispersion might be expected at a fairly high temperature. This, however, is not observed. It is shown that the region of visibly anomalous rotation–dispersion for *iso*butyl tartrate is brought into view by solution of the ester in *s*-tetrachloroethane, this region being, therefore, moved towards a higher temperature and a lower rotation value. In quinoline, the behaviour is very much the same as that of ethyl tartrate. Since the solutions in quinoline darken at temperatures just above 100°, the observations cannot be carried far beyond the minimum values, so, to ascertain what happens beyond this minimum value, the behaviour of *iso*butyl diacetyltartrate in the homogeneous condition was examined. A minimum is found in the graphs for this ester at the ordinary temperature, and since at the minimum the rotation–dispersion is positive, thus corresponding quite closely with what is observed in the neighbourhood of the minimum for ethyl tartrate and *iso*butyl tartrate in quinoline, it is concluded that these minima represent corresponding conditions of the substances, so that the behaviour of *iso*butyl diacetyltartrate between, say, 0° and 200° may be held to represent the behaviour of ethyl tartrate or *iso*butyl tartrate at temperatures from perhaps 300° up to about 500°. On heating *iso*butyl diacetyltartrate beyond the minimum, no further intersection of the graphs takes place; no further region of visibly anomalous rotation-dispersion has been observed. By piecing together the evidence referred to, the author concludes that if these three esters were examined over a wide range they would all show, at low temperatures, negative values of rotation with negative dispersion. As the temperature increased, the temperature–rotation graphs would intersect, giving rise to visibly anomalous rotation–dispersion, continuing to rise to reach maxima at slightly different temperatures. They would then fall again to reach, without further intersection, minimum values, rising thereafter, again without intersection, to attain to new maxima, up to which, in the meantime, they have not been followed. The curves for *iso*butyl diacetyltartrate in *o*-nitrotoluene were found to be remarkable, inasmuch as they exhibit anomalous rotation–dispersion, from which the conclusion is drawn that the effect of this solvent is to displace the minimum of the *iso*butyl diacetyltartrate towards high temperatures, over the maximum corresponding with that actually existing in ethyl tartrate, so as to bring into view the region of anomalous rotation–dispersion corresponding with that which actually exists in ethyl tartrate at the ordinary temperature. It is pointed out that whereas the value of the maximum may be very different, and occur at very different temperatures for a given homogeneous substance and for that substance in solution, or for a derivative of that substance, the rotation value at which the intersection of the temperature–rotation curves for two different colours of light takes place is almost identical. This point is the same as the point of intersection of the two corresponding lines on Armstrong and Walker's characteristic diagram. T. S. PA.

The Influence of Solvents, etc., on the Rotation of Optically Active Compounds. XXII. Rotation Dispersion. THOMAS STEWART PATTERSON (T., 1916, **109**, 1176—1203).—Since, as is shown, the ordinary rotation–dispersion ratios may vary for quite slight changes of external conditions, such as temperature, between +infinity and −infinity, they have obviously very little value. If, however, the dispersion ratio be calculated with respect to the intersection of the corresponding temperature–rotation curves or the intersection of the corresponding lines on Armstrong and Walker's characteristic diagram, this point being regarded as a rational zero for these colours, it is found that the dispersion ratio then shows a very fair constancy throughout a related series of active compounds or for a particular active compound in different solvents or at different temperatures. This is illustrated from data given by Pope and Winmill for benzoyl and various substituted benzoyl, sulphonyl, and naphthoyl derivatives of *l*-tetrahydroquinaldine; by data given by Pickard and Kenyon for methyl-*tert*.-butylcarbinol and *d*-1-naphthyl-*n*-hexylcarbinol, as well as from data from the preceding paper. The manner in which rotation data are likely to lie upon a characteristic diagram in the neighbourhood of a maximum or a minimum in the temperature–rotation curves is discussed. In such cases it appears that the points on the characteristic diagram must return on themselves, whence it seems probable that the data for a given substance should fit approximately on different characteristic diagrams according to the temperature or nature of the solvent. T. S. PA.

The Influence of Solvents, etc., on the Rotation of Optically Active Compounds. XXIII. Anomalous Rotation-Dispersion and Dynamic Isomerism. Thomas Stewart Patterson (T., 1916, **109**, 1204—1228).—The hypothesis of Arndtsen, which has recently been revived by Armstrong and Walker, that anomalous rotation–dispersion is due to the presence of two modifications of one original active compound, is discussed, especially with reference to the assumptions which have to be made to account for the occurrence of these isomerides. The contention of Lowry and Dickson, that ethyl tartrate can be separated by distillation into fractions containing active substances of dissimilar constitution, is held not to be justified by the evidence adduced. It is maintained that if in any case solvent influence on rotation can be shown to exist where mutarotation is equally definitely shown to be absent, Armstrong and Walker's theory may, in general, be regarded as disproved. Now the initial rotation of a mutarotatory compound in solution, such as lævulose, is a datum independent of any consideration regarding mutarotation, and if the initial rotation for such a substance in different solvents be different, it is considered that solvent influence exists independently of dynamic isomerism, and that, therefore, the two phenomena are not necessarily connected. An examination of the mutarotation curves for lævulose in water, in water and ethyl alcohol, and in water and pyridine shows that any solvent effect revealed by the initial rotations is less than the errors of observation of the method. Solvent influences of this kind have, however, been detected by Mackenzie and Ghosh (A., 1915, ii, 301), and others, much more definite, by Lowry, for α-nitrocamphor in various solvents, whence it is concluded that this compound shows a decided solvent influence which has nothing to do with dynamic isomerism, whilst it is also clear from Lowry's data that α-nitrocamphor exhibits a concentration effect as well, thus coming into line with ethyl tartrate. It is also pointed out that it would be very difficult to explain the maxima or minima which are often found in the temperature–rotation curves for active substances, on the assumption that the changes in rotation are due to a variation in the proportions of two dynamic isomerides, one with a high rotation and the other with a low rotation. T. S. Pa.

A Thermostat for Polarimetric [Determinations] particularly during Sugar Inversion at High Temperatures. Theodor Paul (*Zeitsch. physikal. Chem.*, 1916, **91**, 745—755).—A thermostat is described which may be used in connexion with a polarimeter in determining the amount of inversion of sucrose at high temperatures. The main point about the thermostat is that it allows the observation tube, which is made of quartz, to lie horizontally. For mechanical details of both thermostat and observation tube the original must be consulted. The instrument permits of measurements being made at 100°. J. F. S.

Action of Light on the Formation and Decomposition of the Hydrogen Halogen Acids. Alfred Coehn and Karl Stuckardt (*Zeitsch. physikal. Chem.*, 1916, **91**, 722—744).—The authors have investigated the action of light on the gaseous systems hydrogen iodide, hydrogen bromide, hydrogen chloride, and their components. The reactions have been effected by means of a mercury lamp in both quartz and uviol glass apparatus. In all three cases equilibrium has been reached from both sides. In quartz apparatus the decomposition proceeds to the extent of 92·3% in the case of hydrogen iodide, and this is reached in ten minutes; the formation proceeds to 7·6%. In both uviol glass and ordinary glass there is a decomposition of 100% and no formation in the case of hydrogen iodide. With hydrogen bromide there is 100% decomposition in quartz, 20% in uviol glass, and no decomposition in glass. The amount of formation of hydrogen bromide is zero in quartz, 80% in uviol glass, and 100% in glass. In the case of hydrogen chloride there is 0·42% decomposition and 99·58% formation in quartz and 100% formation with no decomposition in uviol glass and ordinary glass. In the case of hydrogen bromide the reaction is complete in four hours and with hydrogen chloride in less than five minutes. The use of the three types of apparatus shows the effect of the different spectral regions in quartz, light down to 220 $\mu\mu$ is active, in uviol glass to 254 $\mu\mu$, and in Jena glass down to 300 $\mu\mu$. The absorption of ultra-violet light by the halogen haloids and the halogens has been determined for various thicknesses of gas. J. F. S.

The Flame Arc in Chemical Manufacture. W. R. Mott and C. W. Bedford (*J. Ind. Eng. Chem.*, 1916, **8**, 1029—1035).—The flame arc at high amperage is, in proportion to the current used, the most efficient source of light known for photo-chemical reactions. The chemical action of the white flame arc through glass on sensitised paper or on *p*-phenylenediamine is three times greater than is that of other coloured flame carbons under similar conditions. The direct-current white flame arc has an action on sensitised paper which can be expressed approximately by the empirical equation: $KC^{1\cdot8}(V-23)$, where C is the current, V arc voltage, and K a constant having a value of 0·0085. The white flame arc is better suited for use with glass vessels than with quartz vessels; at high arc voltages the light and chemical effect increase as the arc voltage is raised, but at a decreasing rate. The use of the white flame arc opens up many new possibilities for controlling and changing chemical reactions (chlorination, bromination, etc.). A means of using an enclosed arc lamp with flame carbons consists in using a shunt around the lamp resistance and solenoid on a direct current, or a reactance coil in shunt around the lamp reactance coil and solenoid on an alterating current. W. P. S.

The Influence of different Gases on the Photoelectricity of Potassium. G. Wiedmann (*Ber. Deut. physikal Ges.*, 1916, **18**, 333—338. Compare A., 1916, ii, 508).—Previous experiments have shown that the photoelectric sensitiveness of potassium is very greatly diminished and the selective photoelectric effect caused to disappear when the metal is freed from gases by repeated distillation in a vacuum. The further investigation of the influence of different gases on such purified potassium indicates that argon and nitrogen produce little change in the sensitiveness of the potassium. Oxygen increases it to a small extent, whilst hydrogen is exceedingly active, and there is no doubt that the photoelectricity of ordinary potassium is almost entirely due to the presence of hydrogen in the metal. This gas appears to be responsible also for the selective effect at $\lambda = 436\ \mu\mu$. H. M. D.

Measurement of the Electrical Conductivity of Solutions at different Frequencies. V. Investigations on the Use of the Vreeland Oscillator and other sources of Current for Conductivity Measurements. W. A. Taylor and S. F. Acree (*J. Amer. Chem. Soc.*, 1916, **38**, 2396—2403. Compare A., 1915, ii, 406).—The authors have examined a number of instruments for producing alternating currents with the object of ascertaining which is most suitable for use in the measurement of the electrical conductivity of solutions. Experiments have been carried out with an induction coil, the 60-cycle city supply (Madison), a Holzer–Cabot wireless alternating current generator, a General Electric type of large generator, a Siemen's–Halske alternating current generator, a Vreeland oscillator working at 500 and 1000 cycles, and the *B* Vreeland oscillator, which works at from 160 to 4200 cycles. Oscillograms of the voltage wave of the current produced in each case have been prepared, and are reproduced in the paper. The authors find that the Vreeland oscillator is the best and most convenient form of instrument for producing alternating current for the present purpose. It is nearly noiseless in action, and gives practically a pure sine voltage wave; it gives a constant frequency which is independent of the variations in the actuating direct current, and it allows of the frequency being changed to anything which may be desired in conductivity work.
J. F. S.

Measurement of the Electrical Conductivity of Solutions at different Frequencies. VI. Investigations on Bridge Methods, Resistances, Cells, Capacities, Inductances, Phase Relations, Precision of Measurements, and a Comparison of the Resistances obtained by the use of Inductance and Capacity Bridges. W. A. Taylor and S. F. Acree (*J. Amer. Chem. Soc.*, 1916, **38**, 2403—2415. See preceding abstract).—A general investigation and discussion on the various factors which affect conductivity determinations of solutions. It is found that the Vreeland oscillator is the most convenient and suitable instrument for producing the alternating current. Curtis coils on porcelain spools should be used for resistances above 10 ohms to prevent errors due to inductance and capacity effects. For the greatest accuracy in balancing a bridge a telephone should be used which can be tuned to any desired frequency and can be attached to a stethoscope. A substitution method as suggested by Curtis for measuring resistance is advantageous, since, by simply regulating the temperature of the variable resistance it prevents errors due to changes in the resistances of the bridge coils, or in the inductance, caused by variations in temperature, and allows of the direct reading of the resistances instead of having to make involved calculations. The constant temperature-bath and the bridge should be earthed to avoid capacity errors. In order to prevent changes in the resistance of the solutions during measurements, the cells should be made with ground-glass joints, which should be below the surface of the thermostat liquid. The electrodes of the cells should be supported by several glass arms to prevent them changing their position, and the leads to the electrodes should be sealed off in glass tubes, so that they may be kept clean, and changes in resistance thus avoided. Solutions should be made up and analysed by weight methods in resistance glass or quartz vessels, and transferred to the conductivity cell under the water of the thermostat. Resistance measurements on a given solution in a given cell can be reproduced to within 0·001%. Resistance measurements on different parts of the same solution in the same cell agree to within 0·01%, even when no precautions are taken in filling the cell. The resistances of aqueous solutions in cells with platinised electrodes do not change appreciably on keeping in the cell for twenty-four hours. Cells with bright electrodes showed changes in resistance of 0·05—0·14% in twenty-four hours. A comparison of the resistances obtained by the use of (1) an inductance, and (2) a condenser to balance the capacity of a cell, shows that the values of the resistances obtained by the two methods are practically the same, the variation being only ±0·001%. J. F. S.

Measurement of the Electrical Conductivity of Solutions at different Frequencies. VII. Investigations on the True and Apparent Resistances, Voltage, Apparent Capacity, Size and Character of Electrodes, Ratio of Inductance Changes to Resistance Changes, and the Relation of Induction and Capacity to Frequency. W. A. Taylor and S. F. Acree (*J. Amer. Chem. Soc.*, 1916, **38**, 2415—2430. See preceding abstracts).—A further paper on the investigation of the various factors which affect the electrical conductivity measurements of solutions. It is shown that there is no measurable change in the resistance of a solution, or the inductance with change in voltage, provided that the cells, solutions, and containers are kept scrupulously clean. If the cells are not clean, however, there is a change in resistance with change of voltage, and this fact may be used as a trustworthy test of the cleanliness of cells. To make accurate conductivity measurements, the cells and methods must be so chosen that the ratios of the resistances for a given solution in two cells, or of two solutions in any cell, are constant to within 0·01%. To achieve this result, electrode effects must be entirely eliminated. From the fact that the ratios of the resistances of *N*/2-, *N*/10-, and *N*/20-solutions of sodium chloride, when measured in cells with 0·5 and 1·0 inch platinised electrodes respectively, did not vary more than 0·01%, which is the experimental error due to all causes, and since there is no measurable change in the resistance of a solution with a change of frequency from 500 to 2000 cycles with platinised electrodes of more than 1 inch in diameter, it follows that 1 inch platinised electrodes give approximately the true electrical resistances of these solutions at the above-mentioned frequencies, and they certainly do at infinite frequencies if the resistance is above 100 ohms.

In cells with bright electrodes there is a change in resistance with change of frequency from 600 to 1000 cycles and higher. This change depends on several factors: (1) As the concentration of any given solution is decreased, and therefore the resistance increased, the change of resistance with change of frequency is decreased. (2) As the area of the electrode surface is increased, the change in resistance with change in frequency is decreased. (3) As the area of the electrode surface is increased, the inductance necessary to obtain a balance is decreased, and hence the apparent capacity of the cell is increased. (4) The higher the apparent capacity of the cell, and therefore the smaller the inductance necessary to balance this capacity, the smaller the change of resistance with change of frequency becomes. Since the apparent capacity of a cell is increased by increasing the electrode surface, platinised electrodes should give the smallest change in resistance with change of frequency, and this is confirmed by the authors' experiments. (5) Solutions of different salts having about the same resistance in the same cell with bright electrodes give approximately the same change in resistance with change in frequency from 600 to 1000 cycles. (6) There is a specific relation between the electrolyte, the electrode material, the character of the electrode surface, and the change of capacity and resistance with change of frequency. This is shown by the fact that for a change of frequency from 600 to 1000 cycles, *N*/10-silver nitrate in a cell with 1 inch bright platinum electrodes gives a change of 0·12%, a similar solution in the same cell with 1 inch rough, silver-plated electrodes gives a change of 0·012%, and a *N*/10-sodium chloride solution in the same cell gives a change of 0·052%. By comparing the resistances of *N*/10- and *N*/20-solutions of sodium chloride in two cells, one of which had bright and the other platinised electrodes 1 inch in diameter, it is shown that the ratio for the cell with bright electrodes is much lower at the lower frequencies than that for the cell with platinised electrodes, but as the frequency is increased, the ratio for the cell with bright electrodes approached that for the cell with platinised electrodes. On extrapolating the resistance for the cell with bright electrodes to infinite frequency, the ratio was found to differ by only 0·004% from that given by the cell with platinised electrodes. This indicates that the true electrical conductivity of solutions can be measured in cells with bright platinum electrodes only at infinite frequency. It is therefore recommended that for conductivity work involving an accuracy of 0·01% a Vreeland oscillator, giving frequencies of 500, 750, 1000, and 1500 cycles, be used, and the corresponding resistances be extrapolated to give that at infinite frequency.

By substitution in the equation $(R_f - R_{f\infty})/L_f f = K$, in which R_f and L_f respectively are the resistance and inductance measurements at a given frequency f, R_∞ is the resistance at infinite frequency, and K a constant, it is possible to calculate R_∞ for any given cell and solution. The values found for R_∞ by this equation differ from those found by extrapolation by only ±0·01% to ±0·025%. It is recommended, since there is a change of resistance with frequency, that all conductivity and resistance measurements should be given at infinite frequency. Saturation of electrodes with hydrogen produces no appreciable change in the capacity of a cell at 60 cycles, which fact shows that the capacity does not arise from a neutral gas layer on the electrodes acting as a condenser. It is probably due to a double layer of ions of the electrolyte and of the solvent at and on the electrodes, and hence to contact potential by these changes of concentration arising from electrolysis. The ratio between the inductance measurements at 600 and 1000 cycles is a constant which has the value 2·66, which shows that the inductance is nearly inversely proportional to the square of the frequency, the ratio for the square of the frequency used being 2·77. As this relation holds true for a leaky condenser, the cell seems to act as a resistance in series with a simple condenser with a leak. As the frequency is increased, the change in resistance of a given solution in a given cell, and also the inductance necessary to balance the capacity of the cell, are decreased, and both approach zero at infinite frequency. It is found that the ratio of the difference in the inductance in millihenries to the difference in the resistance in ohms between 600 and 1000 cycles is constant and equal to 2·00. The electrical capacities of the cells acting as leaky condensers have been measured by different consistent bridge methods. The capacities vary with the solution, size of electrodes, character of surface, and resistance, and range from 10 to 1000 microfarads for bright electrodes, and from 500 to 5000 microfarads for platinised electrodes. J. F. S.

Measurement of Electrolytic Conductivity. I. Theory of the Design of Conductivity Cells. EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1916, **38**, 2431—2460).—A general discussion on the factors involved in the measurement of electrical conductivity. It is pointed out that theory demands the following alterations in the original Kohlrausch method of conductivity measurement: (1) the substitution of a high-frequency generator giving a pure sine wave of a single frequency, in place of the induction coil; (2) the use of a telephone tuned to the frequency employed; (3) the use of resistance units free from inductance and capacity; and (4) a proper and efficient use of the principle of electromagnetic shielding. The author then discusses the arrangement of the Wheatstone bridge and the distribution of the current in the bridge network with the object of ascertaining the most suitable conditions. A general theory of cell design is next considered, from which it is deduced that the area of the cross-section between the electrodes of a conductivity cell must not be less than a certain minimum value, which is completely fixed and determined by the audibility current of the telephone, the time required to make the bridge setting, the lowest specific conductivity which it is desired to include within the range of the cell, and the percentage accuracy demanded in the experiments. This practically means that the conductivity cell should be designed to fit the telephone. Three types of conductivity cells are described for use in measuring: (*a*) water or very dilute solutions; (*b*) dilute solutions; and (*c*) concentrated solutions. In connexion with the various cells, the author discusses: (1) the temperature-coefficient of the cell constant; (2) the choice of materials for the construction of cells; and (3) the elimination of polarisation. J. F. S.

Preparation of Conductivity Water. JAMES KENDALL (*J. Amer. Chem. Soc.*, 1916, **38**, 2460—2466).—A review of previous work on the preparation of conductivity water. It is shown that by distilling tap-water in Jena glass vessels and a tin condenser in contact with air, water of specific conductivity $0{\cdot}9 \times 10^{-6}$ at 25° can be obtained in one distillation. This specific conductivity is the same as that given by a saturated solution of carbonic acid under atmospheric conditions. A permanent lower value for water in contact with air is not possible, since slow absorption of carbon dioxide must take place until equilibrium is established unless air-tight vessels are employed. It is therefore unnecessary in conductivity work to invite the troubles involved in the preparation of purer water than the saturated carbonic acid solution. The aim should rather be to exclude all other conducting impurities except carbonic acid, and make an exact correction for this.

J. F. S.

Galvanic Ennobling of Metals. CH. M. VAN DEVENTER (*Zeitsch. physikal. Chem.*, 1916, **91**, 687—700. Compare A., 1908, ii, 12, 558; 1909, ii, 958; 1910, ii, 179).—The author has examined the ennobling of metals by alcohol–water layers with more exact apparatus than was possible previously. The *E.M.F.* set up in the following types of cells has been measured: $M^{I}|N/15\text{-}H_2SO_4|$ alcohol water$|M^{II}$ and $M^{I}|N/15\text{-}H_2SO_4|$water$|M^{II}$. The pairs of metals examined were Zn^{I}, Zn^{II}; Cd^{I}, Cd^{II}; Zn^{I}, Mg^{II}; Cd^{I}, Mg^{II}; Cd^{I}, Zn^{II}; and Sn^{I}, Cd^{II}. In each case in the first type of cell M^{I} constituted the positive pole, whereas in the second type it constitutes the negative pole. The values found were for the first type, Zn^{I}, Zn^{II} 280 millivolts, Cd^{I}, Cd^{II} 68 millivolts, Zn^{I}, Mg^{II} 425 millivolts, Cd^{I}, Mg^{II} 87 millivolts, Cd^{I}, Zn^{II} 68 millivolts, and Sn^{I}, Cd^{II} 185 millivolts. From the measurements of the cells of the second type, it is calculated that the metals M^{II} have been ennobled by the following amounts in the different cases: Zn^{I}, Zn^{II} *ca.* 200 millivolts, Cd^{I}, Cd^{II} 160 millivolts, Zn^{I}, Mg^{II} 1250 millivolts, Cd^{I}, Mg^{II} 1200 millivolts, Cd^{I} Z^{II} 250 millivolts, and Sn^{I}, Cd^{II} 350 millivolts. It is shown that the ennobled metal becomes coated with a film of metal sulphate which does not dissolve in the alcohol–water mixture, and is a bad conductor of electricity. This ennobled metal is therefore to be regarded as an electrode of the second kind, and consequently the author's theory, previously published, as to the cause of the ennobling is no longer tenable. J. F. S.

Overvoltage Tables. III. Overvoltage and the Periodic Law. EDGAR NEWBERY (T., 1916, **109**, 1107—1117. Compare A., 1916, ii, 598).—Further measurements of cathodic overvoltage in 1*N*-sulphuric acid and 1*N*-sodium hydroxide solutions have been made, and the results show that the value for any particular electrode is closely connected with the position of the metal in the periodic table. Some difficulty is presented in choosing the normal value of the overvoltage, and this difficulty necessitates the investigation of the behaviour of the metal under as many different conditions as possible. In general, cathodic overvoltages in acid solution are more trustworthy than those in alkali solution, for there is only one cation present in the former, whilst the latter contains two.

The cathodic overvoltages fall into nine groups, the last eight of which correspond with groups 1—8 of the periodic table. The first group in the overvoltage table contains elements which show zero overvoltage under certain conditions. These elements are to be found also in one or more of the other groups. When overvoltages corresponding with more than one group are exhibited, the metal in question is known, in nearly all cases, to form compounds in which its valency corresponds with that of the metals of the groups in which it is placed.

Reviewing the overvoltage table as a whole, it is found that an increase of the overvoltage in two equal steps occurs in passing from group 0 to II, and this is followed by a gradual fall in the overvoltage in passing from the second to the eighth group.

Anodic overvoltages do not show the same degree of regularity, and this is probably connected with the fact that the solutions contain more than one anion, whilst a further disturbing factor is the formation of badly conducting oxides or peroxides.

H. M. D.

Effect of Pressure on the Potential of the Hydrogen Electrode. N. EDWARD LOOMIS and S. F. ACREE (*J. Amer. Chem. Soc.*, 1916, **38**, 2391—2396).—A number of experiments have been made to ascertain the effect of pressure on the potential of the hydrogen electrode. For this purpose, the *E.M.F.* of the cell $H_2|Pt,0{\cdot}1N\text{-}HCl|0{\cdot}1KCl,Hg_2Cl_2|Hg$ has been measured for pressures of hydrogen varying between 770·5 mm. and 709·5 mm. It is shown that the potential of the hydrogen electrode, at pressures near the atmospheric pressure, can be represented by the expression $E=RT/2F\,.\log_e H_2/H_2'$, in which H_2 and H_2' are the partial pressures. The average change in potential found is 0·00001751 volt per mm., which is only 0·3% larger than the value

0·00001746 volt calculated by the above formula. The mean value of the above cell at 25° is $0·42723 \pm 0·00003$ volt. J. F. S.

Tables for the Electromotive Estimation of Ion Concentration. J. MATULA (*Koll. Chem. Beihefte*, 1916, **8**, 299—336).—When the hydrogen electrode is combined with the normal calomel electrode, the *E.M.F.* of the cell at 20° and 760 mm. varies from 0·2835 to 0·6921 volt when the concentration of hydrogen ion falls from 1*N* to that of a neutral solution. The first table gives the calculated values of $[\dot{H}]$ for all *E.M.F.*'s within this range, the interval being 0·0001 volt. The second table gives the values of $[OH']$ for *E.M.F.*'s between 0·6921 and 1·1007 volt, which corresponds with the change from a neutral solution to a solution for which $[OH'] = 1N$.

When the pressure and temperature differ from the above values, corrections are supplied by supplementary tables. H. M. D.

Potential of the Mercury Electrode against the Mercurous Ion. G. A. LINHART (*J. Amer. Chem. Soc.*, 1916, **38**, 2356—2361).—The work of Ogg (A., 1899, ii, 14) on the potential of the mercurous ion, using solutions of mercurous nitrate, shows that the mercurous ion is $Hg_2^{\cdot\cdot}$, and that this is ionised further to $Hg^{\cdot}$ ions. The present paper deals with the nature of the mercurous ion, but instead of mercurous nitrate, mercurous perchlorate is used. The advantage of using this salt is that it is hydrolysed to a very slight extent, and the products of hydrolysis are soluble in water (Ley, A., 1904, ii, 465). Potential measurements have been made of cells of the type $Hg|Hg_2(ClO_4)_2HClO_4|$hydrogen electrode, in which the concentrations of perchloric acid varied from 0·0059*N* to 0·0817*N*, and the mercurous perchlorate from 0·0000531*N* to 0·002750*N*. From a large number of measurements it is shown that the best value for the potential of the mercurous electrode is $-0·7928$ volt. No regular deviations from the theoretical value of the *E.M.F.* are observed, from which it is deduced that no appreciable ionisation of the type $Hg_2^{\cdot\cdot} \rightleftharpoons 2Hg^{\cdot}$ occurs even in the most dilute solution examined. J. F. S.

Tenth Normal Hydrochloric Acid Calomel Electrode. N. EDWARD LOOMIS and MERLE R. MEACHAM (*J. Amer. Chem. Soc.*, 1916, **38**, 2310—2316).—A long and careful series of *E.M.F.* measurements have been made of cells of the type $H_2,Pt|0·1NHCl|Hg_2Cl_2|Hg$ at 25° with the object of comparing this cell with the cell $H_2,Pt|0·1NHCl||0·1NKCl|Hg_2Cl_2|Hg$. It is found that the *E.M.F.* has the value $0·3988 \pm 0·0002$ volt at 25°, and that the hydrochloric acid calomel electrode is not as trustworthy as the potassium chloride calomel electrode. The constancy of the hydrochloric acid calomel electrode is greater, the greater the concentration of the acid, and below 0·03*N* the value cannot be depended on. The variations in the *E.M.F.* of this system are probably due to a chemical change in the calomel electrode, by which the potential varies with time. This series of experiments indicates that, within the limits of experimental error, *N*/10-hydrochloric acid and *N*/10-potassium chloride are ionised to the same extent within limits of 1%. J. F. S.

Thermodynamic Properties of Silver and Lead Iodides. HUGH STOTT TAYLOR (*J. Amer. Chem. Soc.*, 1916, **38**, 2295—2310). —A series of *E.M.F.* measurements of cells of the type $Pb|PbI_2|N/x KI|AgI|Ag$ have been made at 0° and 25°. The value of $x=10$ and 20. The object of the measurements was to ascertain whether the assumptions made in the Nernst heat theorem were justifiable, and to ascertain whether the results of Fischer (A., 1912, ii, 536, 1054), Braune and Koref (A., 1914, ii, 536), and Jones and Hartmann (A., 1915, ii, 308) were trustworthy, since these led to diametrically opposite conclusions with regard to the Nernst theorem. The following results were obtained: $N/x=0{\cdot}05$; at 25°, $\epsilon=0{\cdot}21157$ volt; at 0°, $\epsilon=0{\cdot}21475$ volt, whence the temperature-coefficient $=-0{\cdot}000127$ volt per degree and $U=11500$ cals. $N/x=0{\cdot}10$; at 25°, $\epsilon=0{\cdot}21069$ volt; at 0°, $\epsilon=0{\cdot}21415$ volt, whence the temperature-coefficient $=-0{\cdot}000138$ volt per degree and $U=11610$ calories. This gives as the mean heat of reaction of the change $Pb+2AgI=PbI_2+2Ag$, $U=11550\pm50$ cal.

This value agrees well with the value obtained from the best calorimetric data. The above value, when used to test the validity of the assumptions made in the Nernst heat theorem, leads to the conclusion that so far as the present experimental data with regard to specific heats may be employed the assumptions made in the theorem are justified. J. F. S.

Inclusions in the Silver Voltameter. T. W. RICHARDS and F. O. ANDEREGG (*J. Amer. Chem. Soc.*, 1916, **38**, 2044—2046). —A note emphasising the importance of the work of Vinal and Bovard (compare A., 1916, ii, 213) on the inclusion of mother liquors in the crystals deposited in the silver coulometer. The fact that platinum-black has a marked effect on the silver deposited, as shown by Vinal and Bovard, renders necessary the repetition of work by the authors on "volume effect" (compare A., 1915, ii, 81, 308) to see how far this source of error may have invalidated their results. W. G.

The Theory of Electrolytic Ions. VIII. The Mobility of some Inorganic Complex Ions. RICHARD LORENZ and I. POSEN (*Zeitsch. anorg. Chem.*, 1916, **96**, 81—98. Compare A., 1916, ii, 312).—The transport numbers of sixteen cobalt and platinum complex salts have been determined by Hopfgartner's method, using cadmium anodes. The conductivity of the same salts has been determined, and a comparison of the two values leads to constitutions in accordance with Werner's views. The figures are tabulated. C. H. D.

The Ratio of the Boiling Point to the Critical Temperature. W. HERZ (*Zeitsch. anorg. Chem.*, 1916, **96**, 289—290. Compare *ibid.*, 1916, **95**, 253).—It has been shown by Guye (*Bull. Soc. chim.*, 1890, [iii], **4**, 262) that the boiling point of organic liquids under 10—20 mm. pressure is one-half of the critical temperature. It may be assumed that the boiling point under any given pressure is a constant fraction of the critical temperature. C. H. D.

Free Energy of Bromine Compounds. GILBERT N. LEWIS and MERLE RANDALL (*J. Amer. Chem. Soc.*, 1916, **38**, 2348—2356).—A theoretical paper, in which the authors have calculated the free energy of the various forms of bromine, of the bromide and polybromide ions, and of all the known compounds of bromine with hydrogen and oxygen. · In the calculations the available data have been reviewed, and the most probable values used in each case. The following values are obtained at 25° on the assumption that liquid bromine at this temperature possesses zero free energy; gaseous bromine, 755 cal.; solid bromine, 157 cal.; bromine in carbon tetrachloride solution of *N* strength, 389 cal.; aqueous bromine, 977 cal.; dissociated bromine atoms, 22328 cal.; gaseous hydrogen bromide, -12592 cal.; bromide ions (Br'), -24594 cal.; tribromide ions (Br_3'), -25267 cal.; pentabromide ions (Br_5'), -24400 cal.; aqueous hypobromous acid, -19739 cal.; and bromate ions (BrO_3'), 1690 cal. J. F. S.

Transition of Na_2SO_4. ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1916, **91**, 676—686. Compare A., 1916, ii, 551).—A repetition of work previously published (*loc. cit.*). It is shown that no transition occurs at 385° with anhydrous sodium sulphate. The present experiments were made with a lever pressure apparatus, whereas the former pressure apparatus was hydrostatic in its action. The irregularities in the pressure–temperature curve previously obtained are shown to be due to loss of oil from the pressure cylinder. J. F. S.

The Determination of Dissociation Temperatures with the Aid of Cooling and Heating Curves, especially for Cobalto-cobaltic Oxide. J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1916, **96**, 64—70).—The dissociation temperature under atmospheric pressure is determined by heating the oxide in a porcelain tube in a carbon tube furnace. The cooling and heating curves are taken by means of a thermo-couple. Cobaltous oxide gives a smooth cooling curve in nitrogen or carbon dioxide, but in oxygen there is a change of direction at about 700°. On heating, dissociation sets in at 900°, whatever atmosphere be used. This temperature is higher the more compact the oxide. The most compact form, prepared from nitrate, has a dissociation temperature of 959°, Foote and Smith (A., 1908, ii, 847) having found 965° by the statical method. C. H. D.

The Atomic Theory. VIII. Space Filling and Mobility of Complex Inorganic Ions. RICHARD LORENZ and I. POSEN (*Zeitsch. anorg. Chem.*, 1916, **96**, 217—230. Compare A., 1916, ii, 312).—The hypothesis proposed by Lorenz and his collaborators is tested by application to the case of inorganic complex ions of known constitution. For this purpose the density of a number of complex cobalt and platinum salts has been determined, using pure benzene in the pycnometer. For dehydration, the hydrated salts are heated in a vacuum over barium oxide. The density at the absolute zero is calculated by adding 3% to the value at the ordinary temperature, this method being sufficiently accurate, as only the cube root of the molecular volume enters into the calculation of the dimensions of the ions. The electrical conductivities are taken from the authors' previous papers. The volumes of the chlorine and bromine ions are taken from those determined by optical means by Heydweiller (A., 1913, ii, 645), and the mobilities of fifteen inorganic complex ions are then calculated and compared with the experimental values. With the exception of the aquo-salts, all the ions examined fall within two limits, one of which is that given by close tetrahedral packing and the other by van der Waals's equation. Thus these, like the organic ions, move with a velocity corresponding with the law of Stokes and Einstein. Stereochemical conditions are without influence, and no difference is observed between ions with the co-ordination numbers 4 and 6. In many cases, the true volume falls with increasing apparent volume.

C. H. D.

The Kammerlingh Onnes Equation of Condition and the Theory of the Capillary Layer. G. Bakker (*Zeitsch. physikal. Chem.*, 1916, **91**, 641—675. Compare A., 1915, ii, 614, 818; 1916, ii, 553).—A theoretical paper, in which the author further develops his theory of the capillary layer. It is shown by calculation that the theoretical part of the isotherm of Kammerlingh Onnes has a wave form. If ρ_1 and ρ_2 are respectively the densities of liquid and vapour in equilibrium and $\mu(\rho_1)$ and $\mu(\rho_2)$ the values of the corresponding thermodynamic potentials, then it is known that $\mu(\rho_1)=\mu(\rho_2)$. The author's theory then states that if between the liquid and vapour phase there is an horizontal capillary layer, $\mu(\rho_1)=\mu(\rho_2)=\mu[(\rho_1+\rho_2)/2]$. This can be expressed as follows: The density of that point on the labile portion of the isotherm where the thermodynamic potential has the same value as the usual liquid and vapour phase is the mean of the densities of the liquid and vapour. This statement has been proved in the case of carbon dioxide, where it is shown that at 0° $\mu(\rho_1)=3{\cdot}2616$, $\mu(\rho_2)=3{\cdot}3787$, and $\mu[(\rho_1+\rho_2)/2]=3{\cdot}2516$; other values are given for 10°, 20°, and 30°, all of which, like the above figures, show the truth of the statement. Hence, where the equation of condition fulfils the relationship $\mu(\rho_1)=\mu(\rho_2)$ there also are the conditions of the author's theory fulfilled. The radius of the smallest particle of vapour of carbon dioxide at 20° is calculated, and the value $R_{\text{min.}}=2{\cdot}25$ millimicrons found; a similar value for the smallest drop of liquid at the same temperature is found to be $R_{\text{min.}}=2$ millimicrons. It has been previously shown (*loc. cit.*) that the thickness of the capillary layer of carbon dioxide at 20° is $\zeta=2{\cdot}5\ \mu\mu$. Hence it follows that these two quantities are of the same order.

The same quantities have been deduced for 0°, and practically identical values obtained. If ρ_1 and ρ_2 are the densities of the liquid and vapour phases respectively, and ρ that of the capillary layer, ζ and R respectively the thickness and radius of the capillary layer, then for every curved capillary layer the following relationships hold: $[\rho-(\rho_1+\rho_2)/2]/\rho_1-\rho_2=\mp 5\zeta/24R$ and $[p_T-(p_1+p_2)/2]/p_1-p_2=\mp(R/2\zeta+5\zeta/24R)$, where p_T is the pressure in the long direction of the capillary layer and p_1 and p_2 the pressures of the homogeneous phases. The negative sign applies to liquid drops, and the positive sign to vapour bubbles. In the case of a horizontal capillary layer, $R=\infty$ and $p_1=p_2$, and the equations become $[\rho-(\rho_1+\rho_2)/2]/(\rho_1-\rho_2)=0$ or $\rho=(\rho_1+\rho_2)/2$.

As a consequence of the author's theory, the pressure in the long direction of a capillary layer (horizontal or curved) has the same value as the pressure at that point in the labile part of the theoretical isotherm where the thermodynamic potential has the same value as in the homogeneous phases which the capillary layer separates. It is shown by calculations that the Kammerlingh Onnes equation of condition confirms this deduction. If in an isothermal diagram the pressure (in the long direction) and the specific volume of every curved capillary layer are plotted, then the curve drawn through these points represents the labile portion of the isotherm for the given temperature. J. F. S.

Osmotic Pressure of Colloids. VI. Osmotic Pressure of Gelatin. WILHELM BILTZ, GÜNTHER BUGGE, and LUDWIG MEHLER (*Zeitsch. physikal. Chem.*, 1916, **91**, 705—721. Compare A., 1910, ii, 22, 673; 1911, ii, 702; 1913, i, 593, 832).—The authors have determined the osmotic pressure of solutions of nine varieties of gelatin, at 20°, at concentrations varying from 0·042% to 0·265%. From the osmotic pressure values the molecular weight has been calculated, and found to vary from 5500 to 31,000 for the different varieties. It is shown that the mineral matter contained in the gelatin has no influence on the osmotic pressure. A series of gold numbers was determined for the various samples, and a series of viscosity measurements was made for 0·05%, 0·10%, and 0·20% solutions of each variety after the solution had been made up twelve hours, twenty-four hours, and seventy-two hours. It is shown that, just as in the case of dextrin, the larger the molecular weight the better the protective action, and the greater the molecular weight the greater the viscosity. The authors therefore put forward as a general rule the statement: That in highly dispersed colloids the viscosity increases with increasing size of the particles, and the gold number, where such can be determined, decreases with increasing size of the particles. In an addendum details are given of the osmotic pressure of protein from horse serum. It is shown that the molecular weight is about 53,500. J. F. S.

Solubilities of Liquids in Liquids. Partition of the Lower Alcohols between Water and Cotton-seed Oil. B. B. WROTH and E. EMMET REID (*J. Amer. Chem. Soc.*, 1916, **38**, 2316—2325).—The solubilities of methyl, ethyl, propyl, *iso*butyl, and *iso*amyl alcohols have been determined in cotton-seed oil by calculation from the partition-coefficient between water and cotton-seed oil. If S_a and S_b represent respectively the solubilities of the alcohol in water and oil, C_a and C_b the concentrations in the same two solvents at equilibrium, and k the partition-coefficient, then $S_a/S_b=k=C_a/C_b$. The values of C_a and C_b were determined experimentally, and k calculated, and then either S_a or S_b was experimentally determined. The analysis of the two layers after partition was effected by means of an interferometer. The following values of k were obtained at 25°: methyl alcohol, 103·6: ethyl alcohol, 28·3; propyl alcohol, 6·41; *iso*butyl alcohol, 1·70; and *iso*amyl alcohol, 0·47. Methyl alcohol dissolves to the extent of 4·84 grams in 100 c.c. of cotton-seed oil, ethyl alcohol 21·2 grams in 100 c.c. of oil, and propyl, *iso*butyl, and *iso*amyl alcohols are soluble in all proportions. On calculating the solubility of methyl and ethyl alcohols in water from the above data, the figures 505 and 600 grams per 100 c.c. are obtained respectively. The authors point out that these figures represent ideal solubilities which could be realised if water and alcohol were separated by a semipermeable membrane through which only the alcohol molecules could pass.

J. F. S.

Crystal Stereochemistry. F. RINNE (*Zeitsch. anorg. Chem.*, 1916, **96**, [iv], 317—352).—The representations of crystal structures which have been deduced by the *X*-ray method, such as those put forward by W. H. and W. L. Bragg for rock-salt, zinc blende, pyrites, and calcspar, are to be regarded as crystal stereochemical formulæ. The conception of the crystal structure as purely atomic is held to be false (compare Niggli, A., 1916, ii, 300). Structural groups of atoms are clearly discernible, for instance, in the structures of calcite and corundum, and physico-chemical considerations clearly point to the existence of combination of a rigid character between the mathematically-considered distinct particles. The number of molecules contained within the unit space-lattice, however, bears no relation to the molecular complexity of the substance in the crystal. A crystal may be built up of similar, similarly orientated atoms, as in diamond; in other cases the atoms may appear in symmetrically distributed groups; or, finally, the structure may be partitionable into atomic complexes of a molecular character. The atomistic conception of Groth and the molecular theory of Bravais can thus be reconciled.

The forces of affinity between the atoms in the crystal can be supposed to act along the straight lines joining neighbouring particles, either the whole or a fraction of a valency being directed along each line. Thus in zinc blende, a zinc atom is tetrahedrally disposed towards four sulphur atoms, and may distribute its two valencies equally in the four directions towards these atoms. The affinities of the bivalent sulphur atom are similarly split up between four zinc atoms. In sodium chloride the affinity of each sodium or chlorine atom may be supposed to be partitioned among six neighbours. A connexion is traceable between such considerations and

Werner's theory of principal and subsidiary valencies (compare Pfeiffer, A., 1916, ii, 228).

The Laue diagram is of use in determining the principal zones and zone axes of a crystal structure, and to some extent the symmetry, although it only distinguishes eleven of the thirty-two classes. It also shows the relation between the forms of a polymorphous substance, between isomorphous substances, or between morphotropically related substances, such as the monoclinic and triclinic felspars.

The crystalline state is characterised by a three-dimensional periodic and straight-line orientation of similar particles, together with the capability of an indefinite extension of the structure, according to the same periodicity, in any direction. Amorphous substances lack this combination of properties. Liquid crystals occupy an intermediate position. Here the intermolecular forces are not strong enough to build up a space-lattice structure, but at the same time are sufficient to bring about a regular orientation of the particles with respect to a molecular axis. E. H. R.

Constitution and Fundamental Properties of Solids and Liquids. I. Solids. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1916, **38**, 2221—2295).—A long, theoretical paper, in which the work of Bragg is considered from the point of view of chemistry and its relation to the theories of chemical constitution, due to Werner, Stark, J. J. Thomson, and Lewis, and discussed in considerable detail. From the discussion the conclusion is drawn that the substances which have been studied by means of their *X*-ray spectra are not representative of compounds in general, since only polar compounds were considered. Solid polar compounds are, as a rule, built up of atoms bound together by residual valencies, and in these cases the whole crystal must be regarded as a single molecule. Solid, non-polar compounds consist, in general, of "group molecules," in which the atoms are held together by primary valencies. These group molecules are bound together by secondary valencies to form a large "crystal molecule," which includes the whole solid mass.

There is at present no justification for dividing intermolecular or interatomic forces into physical and chemical forces. It is better to regard all such forces as strictly chemical. Evaporation, condensation, solution, crystallisation, adsorption, surface tension, etc., should all be regarded as typical chemical phenomena, and it is the object of the present paper to show that these processes can be so treated. From a consideration of specific heat, compressibility, and coefficient of expansion it is deduced that collisions do not occur between the atoms of solids, but that these move about equilibrium positions under the influence of both attractive and repulsive forces. The "time of relaxation" of the atoms of solids is calculated approximately from the thermal conductivity, and is shown to be of the order 10^{-7}—10^{-14} second. Somewhat similar results are obtained from a calculation based on the rate of evaporation in a vacuum. Consequently, the time required by an atom of a solid to reach thermal equilibrium with the surrounding atoms is very small in comparison with the time required to make a single oscillation about its equilibrium position. The oscillations are thus very strongly damped. Since solid substances are, in general, held together by residual valencies rather than by primary valencies, there are few limitations to the number of compounds which can exist in the solid state. Most of these compounds do not show a composition which could be predicted from the valency rules. A discussion is entered into on this point in the case of intermetallic compounds, minerals, solid solutions, and glasses. From a consideration of compressibility it is deduced that the attractive forces between atoms usually reach a maximum intensity when the distance between adjacent atoms in solids is increased by about $0{\cdot}6 \times 10^{-8}$ cm., that is, by about 10—30% of the normal distance. Since energy must be expended in breaking apart a solid, the surfaces of solids must contain more potential energy than do the corresponding number of atoms in the interior. Since this potential energy is probably electromagnetic energy in the field between the atoms, the interatomic forces are more intense on the surface than in the interior. This intense surface field of force (unsaturated chemical affinity) is one of the causes of the phenomena of condensation and adsorption. Because of the small time of relaxation and because an atom approaching the surface is attracted by many atoms and later is repelled by a few atoms, it follows that the surfaces of solids are almost entirely inelastic to collisions of molecules impinging on them. As a result, nearly every molecule or atom striking a solid surface condenses, no matter what the temperature may be. Whilst condensed, it is held to the surface by forces similar to those holding solids together (primary or secondary valencies). At high temperatures evaporation may take place immediately after condensation, but at lower temperatures the condensed atom or molecule may remain indefinitely. A general discussion of sublimation is entered into. It is shown that the rate of evaporation, m, of a substance in a high vacuum is related to the pressure of the saturated vapour, p, by the expression $m=(pM/2\pi RT)^{\frac{1}{2}}$. Red phosphorus is not in agreement with this relationship.

The mechanism of the dissociation of a solid, such as calcium carbonate, is discussed. It is shown that when, according to the phase rule, separate phases of constant composition are present, the reaction must take place at the boundaries of these phases. This kinetic interpretation of the phase rule indicates the distinction between reactions in which solid solutions are formed and those in which separate phases appear. This theory offers an explanation for the fact that hydrated crystals frequently fail to effloresce until scratched, and for the fact that completely dehydrated substances often absorb moisture with difficulty.

Adsorption is a direct consequence of the time lag between the condensation and subsequent evaporation of molecules; the adsorbed substance may be held to the surface by either primary or residual valencies; in either case it is better to regard the phenomena as entirely chemical in character. A large number of experimental results are given to prove that adsorption is very frequently the result of the strongest kind of chemical union (primary valency) between the atoms of the adsorbed substance and the atoms of the solid.

It is shown that the action of a typical catalyst poison depends on the formation of a very stable film, one atom thick, over the surface of the catalyst. The chemical activity of a solid surface depends on (1) the nature of, (2) the arrangement of, and (3) the spacing of the atoms forming the surface layer. There is a very close relation between the chemical activity of a surface and the electron emission from it.

A quantitative development of this theory of heterogeneous reactions is given, and a law of surface action, analogous to, but different from, the law of mass action, is proposed. This theory is in accord with, and affords an explanation of, Reichinstein's "Constant Sum Hypothesis." An application of this theory is made in the cases of heterogeneous gas reactions and to enzyme action.

J. F. S.

Protective Colloids. Radix Althaeae as Protective Colloid. A. Gutbier and G. L. Weise (*Kolloid Zeitsch.*, 1916, **19**, 177—191. Compare A., 1916, ii, 556).—The preparation and general properties of the colloidal solutions obtained by extracting the roots of marsh mallow are described. It is difficult to obtain optically clear extracts by filtration, but the addition of ethyl acetate is found to be of great assistance in the achievement of this result, and this reagent at the same time increases very markedly the stability of the solutions.

The behaviour of the solutions on dialysis, the phenomena of ageing, the influence of concentration and of electrolytes on the stability are described in detail. In an electrical field, the colloidal particles move to the anode, and this phenomenon is independent of the previous history of the solution. H. M. D.

Relation between the Chemical Constitution of Organic Compounds and their Capacity to Coagulate Acid Gold Hydrosols. John A. Gann (*Koll. Chem. Beihefte*, 1916, **8**, 251—298).—The coagulating capacity of a large number of substances has been examined by measuring the "gold number," the substances investigated including albumoses, peptones, polypeptides, dyes, alkaloids, amines, and various heterocyclic compounds.

The results obtained show that the coagulating capacity of these nitrogen compounds depends on the presence of basic nitrogen groups, but that, apart from this, it varies considerably with the constitution of the substance. The auxochromic hydroxyl group increases the activity, although its effect is less marked than that of the amino-group. Certain configurations, such as those peculiar to the azines, thioazines, oxazines, and acridine derivatives also increase the coagulating activity, whilst chromophoric groups have the opposite effect, and this is the more pronounced the more strongly acid the chromophoric group is. The less active a substance is found to be, the greater is the effect which is produced by the introduction of a new group.

With certain exceptions, the gold number for a particular substance is almost independent of the concentration of the coagulant. It varies, however, to some extent with the degree of dispersity, the concentration, and the acidity or alkalinity of the gold solution.

The coagulation process is in most cases to be regarded as brought about by ions, although in the case of the albumins it may be due to the mutual interaction of oppositely charged colloidal particles. The behaviour of gelatin shows that it may act either as a protective colloid or as a coagulant, and the actual results which have been obtained with this substance are discussed in detail with special reference to its amphoteric character.

H. M. D.

The Phenomena of "Clot" Formation. IV. The Diphasic Erosive Action of Salts on the Cholate Gel. S. B. Schryver and Mary Hewlett (*Proc. Roy. Soc.*, 1916, [*B*], **89**, 361—372. Compare A., 1916, i, 448).—The erosive action of salts on the cholate gel containing added salts was investigated. If the concentration of the salts in the eroding solution are plotted as abscissæ and the amount of erosion as ordinates, a curve of diphasic character is obtained. The amount of erosion increases with increasing concentration to a maximum, after which it diminishes to a minimum; with further increase in concentration, the erosion increases continuously. The portion of the curve between the two minimal points is designated the "zone of instability." The breadth of this zone, and the amount of erosion within it, are functions of the amount of salt added to the gel. The amount of erosion and the breadth of the "zone of instability" vary with different eroding salts. The order of the action of chlorides is as follows: $LiCl > NaCl$ (generally) $> MgCl_2 > KCl$. This is the order of their action in increasing the permeability of vegetable cells. The action of sodium salts of organic acids was also investigated, and in all cases the general form of the curves was the same (diphasic). The antagonistic action of calcium salts was also examined, and it was found that relatively more calcium was necessary to antagonise the erosive action in the "zone of instability" than in higher concentration. The various physicochemical factors involved are discussed by the authors, and also the bearing of the results on certain biological problems.

S. B. S.

Fibrin and its Relationship to Certain Questions in Biology and the Chemistry of Colloids. X. The Two Kinds of Fibrin Sols and their Relations to the Conceptions of Colloidal Solutions. E. Hekma (*Biochem. Zeitsch.*, 1916, **77**, 249—256).—Attention is directed to the distinction between the two kinds of sols, one of which is formed from solid fibrin particles in the very finest state of subdivision which exist without water of imbibition, whilst the other is formed from particles of semi-fluid form with water of imbibition, which is taken up by fibrin in the presence of alkalis and acids. S. B. S.

Fibrin in its Relationship to Certain Questions in Biology and the Chemistry of Colloids. XI. The Three Kinds of Fibrin Gels. E. HEKMA (*Biochem. Zeitsch.*, 1916, **77**, 256—267).—A discussion of the processes of gel formation.

S. B. S.

The Law of Reaction Velocity and of Equilibrium in Gases. The Additivity of $C_v - \frac{3}{2}R$. New Determinations of the Integration Constants and of the Molecular Diameter. MAX TRAUTZ (*Zeitsch. anorg. Chem.*, 1916, **96**, 1—28. Compare A., 1914, ii, 457; 1916, ii, 304).—It is assumed that when two molecules collide in an ideal gas, either the collision lasts only for a very short time, when no result is produced, or else it lasts for a time comparable with that between the collisions, in which case a chemical reaction takes place. Starting from the usual assumptions of thermodynamics and of the theory of gases, together with the author's principle of the additivity of the internal atomic heats, it is possible to calculate the integration constants of gas reactions and to compare them with the experimental values. All reactions in gases may be regarded as of the first or second order, all reactions of apparently higher order being regarded as due to successive collisions of pairs of molecules.

These considerations are applied to all the gas reactions of which the velocities have been determined. The constant K is found to have an average value of 10^{12} mols. per c.c. per second, but the values for different reactions given vary between $2{\cdot}5 \times 10^{11}$ and 10^{16}. The heat of activation, q_0, is also found to be constant. For the case of nitrosyl chloride, the molecular diameter is calculated to be $3{\cdot}45 \times 10^{-8}$ cm. C. H. D.

The Velocity of Hydration of Metaphosphoric Acid. II. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1916, **96**, 99—107. Compare A., 1911, ii, 974).—The molecular weight of orthophosphoric acid in dilute glacial acetic acid solution corresponds with the simplest formula. The hydration of metaphosphoric acid is affected by the presence of either acetic or sulphuric acid in the solution, and the results suggest that the unimolecular acid has the greater velocity of hydration. The meta-acid is rapidly hydrated by dissolving in concentrated hydrochloric or nitric acid. The course of the reaction when phosphoric oxide is dissolved in water has been followed by titration with sodium hydroxide, using methyl-orange and phenolphthalein as indicators. Only the meta-acid is obtained in ice-cooled water. The results obtained in previous papers are summarised. C. H. D.

The Reaction of both the Ions and the Non-ionised Forms of Acids, Bases, and Salts : the Reaction of Methyl Iodide with Sodium, Potassium, and Lithium Ethoxides at 0°. BESSIE M. BROWN and S. F. ACREE (*J. Amer. Chem. Soc.*, 1916, **38**, 2145—2156. Compare Robertson, A., 1915, ii, 406, 681; Taylor and Acree, A., 1916, ii, 423).—A study of the rates of reaction between methyl iodide and sodium, potassium, and lithium ethoxides at 0°, the concentrations of the ethoxides varying between N/1 and N/32. The activity, K_i, of unit concentrations of the ethoxide ion, calculated from the data obtained, was the same whichever ethoxide was used, and the average value was 0·0051 at 0°. The value, K_m, for the non-ionised molecule varied with the ethoxide, being about 0·0030 for sodium ethoxide, 0·0034 for potassium ethoxide, and 0·0020 for lithium ethoxide. The solutions used being concentrated, the values obtained will need to be corrected later for the various physical constants, such as viscosity, specific gravity, etc., which are modified by the different substances present. The results obtained support the general theory as to the activity of both the ions and the non-ionised portion of acids, bases, and salts. W. G.

The Hydrolysis of Hexahydropyrimidine. GERALD E. K. BRANCH (*J. Amer. Chem. Soc.*, 1916, **38**, 2466—2474. Compare Titherley and Branch, T., 1913, **103**, 330).—In the first part of the paper the author discusses the effect of the hydrogen ion on additive reactions of an allelotropic mixture, which involves a tautomeric shift about a nitrogen atom, and points out that in such cases the hydrogen ion may be expected to act as a negative catalyst. The rate of hydrolysis of hexahydropyrimidine was measured at two different temperatures and with varying hydrogen-ion concentrations, the results obtained being in agreement with the theory. The reaction was found to have a high temperature-coefficient, the mean values of K_2 found being $3·67 . 10^{-3}$ at 25° and $1·46 . 10^{-3}$ at 18·4°. Alcohol increased the rate of hydrolysis of hexahydropyrimidine. At low concentrations, sodium chloride increased the rate of this reaction, but at higher concentrations it acted as a negative catalyst. W. G.

A Period of Induction in the Dehydration of some Crystalline Hydrates. WILLIAM NORMAN RAE (T., 1916, **109**, 1229—1236).—The rate of dehydration of crystals of copper sulphate pentahydrate has been investigated with the object of determining the cause of the induction period which is associated with the process. Mechanical stirring of the finely powdered crystals increases the initial rate of dehydration, and inoculation with crystals of the trihydrate produces the same effect. In the later stages, the progress of the dehydration is in approximate agreement with the equation for a unimolecular reaction.

The results obtained in respect of the initial period suggest a close analogy with the behaviour of supersaturated solutions, and if this view is correct, it may be that the induction period is to be referred to the relatively high vapour pressure of very small particles of copper sulphate trihydrate as compared with the vapour pressure of larger particles. By taking into account the influence of the size of the particles on the vapour pressure of the lower hydrate, it is unnecessary to assume the intermediate formation of an unstable amorphous form, a view advanced by Partington (T., 1911, **99**, 466) to account for his observations on the variation in the vapour pressure of crystalline hydrates. H. M. D.

Saponification of some Esters of Pyrroledicarboxylic Acid at 50°. G. KORSCHUN and A. GOUNDER (*Bull. Soc. chim.*, 1916, [iv], **19**, 366—392; *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 637—667).—A continuation of previous work (compare A., 1916, i, 606; ii, 525). Starting with ethyl 2:5-dimethylpyrrole-3:4-dicarboxylate, the authors have examined the effect of introducing a methyl group into position 1, and then substituting this in turn by an amino-, a carbamido-, and a phenyl group on the rate of saponification of the first and second carbethoxy-groups by potassium hydroxide at 50°. The saponification constant for each group is given in each case, but as the concentrations of alkali used vary, these cannot be tabulated. The introduction of the methyl group into position 1 increases the ease of saponification of the first carbethoxy-group of the di-ester. The introduction of the amino-group into position 1 renders it more difficult to saponify the monoethyl ester than in the case of either the trimethyl- or the dimethyl-pyrroledicarboxylic acid monoethyl ester. The results obtained when a carbamido-group is introduced into position, are difficult to interpret, and require further work to be done with the di-ester. The results obtained with a phenyl group in position 1 are unsatisfactory, owing to the instability of the monoethyl ester of 1-phenyl-2:5-dimethylpyrrole-3:4-dicarboxylic acid.

Determinations were also made in the cases of diethyl 2:5-diphenylpyrrole-3:4-dicarboxylate, diethyl 2:4-dimethylpyrrole-3:5-dicarboxylate, and 3-carbethoxy-2:4-dimethylpyrrole-5-carboxylic acid. W. G.

Dissociation of Salicylic Acid. J. A. CHRISTIANSEN (*Zeitsch. physikal. Chem.*, 1916, **91**, 701—704. Compare Bauer and Orthner, A., 1916, ii, 232).—The author has repeated the experiments of Bauer and Orthner on the dissociation of salicylic acid. It is shown that at 203° salicylic acid is completely dissociated, whereas it had previously been stated by Bauer and Orthner that the reaction only occurred to the extent of 25% at this temperature. The present author is of the opinion that the low result is due to the shortness of duration of the experiments. J. F. S.

Catalysis of Hydrogen and Oxygen Mixtures at the Ordinary Temperature by Moistened Contact Substances. K. A. HOFMANN and RALF EBERT (*Ber.*, 1916, **49**, 2369—2389).—A summary of some experiments on the union of hydrogen with oxygen in the presence of various contact catalysts is given. Most of the conclusions have been given before in many other papers by one of the authors in recent years, and have been embodied in his method for estimating hydrogen (see A., 1916, ii, 636). The points of particular interest may be stated again.

The catalysis of the union of hydrogen with oxygen at metallic surfaces is an electromotive process, and the reaction is comparable with that in the gas chain of a Groves's cell. Oxygen takes a much longer time to acquire the necessary potential than hydrogen does at platinum, iridium, or palladium surfaces, and the combination of hydrogen with oxygen in a mixture can therefore be accelerated by a preliminary loading of the contact substance with oxygen. The oxidation-potential of oxygen is higher in an acid medium than in an alkaline or neutral one.

It is particularly emphasised that it is not sufficient to "activate" one reagent in order to accelerate a reaction. Each participant must be activated. For this purpose, combinations of catalysts must be used, the most powerful in the case of hydrogen and oxygen being palladium and small quantities of most finely divided palladium in the presence of sodium hydrogen carbonate. The addition of hydrogen or oxygen "carriers" is not advisable, as they will so reduce the potential of the oxygen or the hydrogen, as the case may be, that their influence may be more than nullified.

J. C. W.

The Dual Theory of Acid Catalysis. A Comparison of the Activities of certain Strong Acids. HARRY MEDFORTH DAWSON and THOMAS WILLIAM CRANN (T., 1916, **109**, 1262—1277. Compare T., 1913, **103**, 2135; 1915, **107**, 1426).—With a view to the further examination of the dual theory of acid catalysis, measurements have been made of the rate of isomeric change of acetone under the catalytic influence of hydrobromic, trichloroacetic, trichlorobutyric, and *p*-toluenesulphonic acids at different concentrations.

The velocity-coefficients of the ionised acid, k_H, and the non-ionised acid, k_M, are derived from the equations $k_H = V_1(1-\alpha_1) - V_2(1-\alpha_2)/\alpha_1 - \alpha_2$ and $k_M = V_2\alpha_1 - V_1\alpha_2/\alpha_1 - \alpha_2$, in which V_1 and V_2 are the equivalent velocities of the reaction, and α_1 and α_2 the corresponding degrees of ionisation of the acid. The α-values required were obtained from conductivity data.

The weighted mean values of k_H and k_M are employed to calculate the velocities of reaction, and the results are shown to be in satisfactory agreement with the measured velocities, thus affording further evidence in favour of the dual activity of the acids.

The ratio k_M/k_H is in all cases greater than unity, and this shows that the acid is more active in the non-ionised condition, a result previously obtained for hydrochloric acid. On the assumption that $\alpha = \Lambda/\Lambda_\infty$, the value of the ratio decreases in the order hydrochloric, hydrobromic, trichloroacetic, *p*-toluenesulphonic, and trichlorobutyric acids. For trichlorobutyric acid, k_M/k_H is nearly equal to unity, and it follows that the catalytic activity of this acid is determined solely by the concentration and is independent of the degree of ionisation.

When the k_M/k_H values are compared with those obtained by other observers in experiments on the hydrolysis of ethyl acetate and sucrose, very considerable differences are found in the case of trichloroacetic and trichlorobutyric acids. For the latter acid, the two values of k_M/k_H are approximately as 20 : 1, and it would therefore seem that the magnitude of the ratio varies according to the nature of the catalysed reaction.

Incidentally, it is shown that the dual hypothesis is in harmony with Arrhenius's equation, $v=k_Hca+k'_M(ca)^2$, so long as weak acids are in question.

The fact that the catalytic activity of the strong acids, as measured by the equivalent velocity, V, may be represented by the equation $V=V_0+a\sqrt[3]{c}$, in which V_0 is the velocity for $c=0$ and a is a constant (Snethlage, A., 1915, ii, 615, 825), is shown to be a consequence of the dual hypothesis, and is to be attributed to the circumstance that the conductivity varies with the concentration of the acid in fairly close agreement with Kohlrausch's equation, $\Lambda=\Lambda_\infty-b\sqrt[3]{c}$. H. M. D.

The Atomic Weights. O. D. Chwolson (*Bull. Acad. Imp. Sci. Petrograd,* 1915, 1841—1852).—A theoretical paper in which the author considers how near the atomic weights of the elements approach to some multiple of four (atomic weight of helium). By arranging the numbers under differing groups, allowing for possible errors in the values used (Landolt's tables, 1912) the author arrives at the view that the atomic weights are considerably condensed around numbers of the type $4n$, and that the number of values coming between $4n$ and $4n-2$ considerably exceeds those coming between $4n$ and $4n+2$. W. G.

The Law of the Periodicity of the Elements, and the Natural Periodic System. S. Silbermann (*Ber.*, 1916, **49**, 2219—2222).—In connexion with the larger question of the "Creation, and the origin of energy and matter," the author has developed the idea that the inert gases are the parent substances of all the elements. He regards argon as a mixture of a gas with the atomic weight 36·4 and another with the weight 153. If the elements are grouped in the order of their atomic weights in periods from one amphoteric element to the next (H to Li, Gl to Mg, Al to Sc, Ti to Yt, Zr to Ce, Pr to Tm, Yb to U), each period will be found to contain an inert gas, including the unknown gas with atomic weight 153. The weights can be so plotted that the inert gases fall on a vertical line, when the other elements will fall on parallel straight lines which cross this. Immediately to the left of the line will be found the most electronegative elements, to the right the electropositive, and these characteristics will be found to become less and less pronounced the more remote the element is from the line. Connecting elements of one chemical family by other lines, it becomes apparent that the most perfect agreement among the elements of a particular family is when the connecting line approaches more nearly to a straight line parallel to the inert gas line. A diagram which embodies these features is given. J. C. W.

Molecular Weight Determinations in Bromine by the Air-current Method. Robert Wright (T., 1916, **109**, 1134—1139).—The vapour pressures of pure bromine and of bromine containing foreign substances dissolved in it are measured at the same temperature by the air-current method. The apparatus was designed so that the bromine vapour can only come into contact with glass and the absorbing solution. Molecular weights calculated from the Raoult equation gave for bromoform, antimony tribromide, stannic bromide, and iodine monobromide values corresponding with the empirical formulæ. The value for sulphur shows that it is present in the form of diatomic molecules.
H. M. D.

The "Cyclic Theory" of the Constitution of Complex Inorganic Compounds: A Criticism. Eustace Ebenezer Turner (T., 1916, **109**, 1130—1134).—A criticism of Friend's views on valency (T., 1908, **93**, 260, 1006). H. M. D.

Double Bond and the Electron Theory. L. Spiegel (*Biochem. Zeitsch.*, 1916, **76**, 313).—A claim for priority.
S. B. S.

New Application of the Bunsen Valve. Alan Leighton (*J. Ind. Eng. Chem.*, 1916, **8**, 1037—1038).—A Bunsen valve may be inserted in the tube connecting a water-pump with a vessel from which the air is being exhausted; any back-flow of water from the pump to the vessel, due to accidental decrease in the water pressure, is thus prevented. Thick-walled caoutchouc tubing should be used in constructing the valve or the modification of the Bunsen valve described by Kreider (A., 1896, ii, 161) may be employed.
W. P. S.

An Electrically Heated Vacuum Desiccator. T. Brailsford Robertson and Carl L. A. Schmidt (*J. Biol. Chem.*, 1916, **27**, 429—431).—The apparatus consists of a double-walled copper chamber maintained at the desired temperature by electrical heating elements, for a description of which the original paper must be consulted. H. W. B.

Simple Mercury Sealed Ether Still. O. C. Smith and D. G. Morgan (*J. Ind. Eng. Chem.*, 1916, **8**, 1039).—The distillation flask is closed by a cork, which is inserted so that its upper surface is a short distance below the top of the neck. This cork carries a short piece of glass tubing, over the top of which is fitted the end of the condenser. Mercury is now poured into the neck of the flask until the space above the cork is filled. A flask similarly fitted serves as the receiver, but the cork closing this flask carries a second tube, which is connected with a reflux apparatus to prevent loss of ether vapour. The distillation flask is heated by an ordinary electric bulb fitted below a tripod supporting the flask, and is surrounded by a metal shield. W. P. S.

Inorganic Chemistry.

Apparatus for the Recovery of Bromine. C. H. Collings (*Chem. News*, 1916, **114**, 259—260).—Waste liquors from estimations of urea by the hypobromite method are collected, and measured quantities are decomposed by hydrochloric acid in a suitable bottle; the liberated bromine is absorbed in a vessel containing sodium hydroxide solution, and sodium hypobromite is thus re-formed. A current of air, passed previously through sodium hydroxide solution, is drawn through the apparatus to carry over the bromine vapour, tapped funnels are provided for introducing more waste liquor and sodium hydroxide respectively, and the bottle and absorption apparatus are fitted with siphons for drawing off their contents when necessary. W. P. S.

Colloidal Iodine. H. Bordier and G. Roy (*Compt. rend.*, 1916, **163**, 567—569. Compare A., 1916, i, 630, ii, 547).—Ultramicroscopic examination confirms the view (*loc. cit.*) that iodine in pure water is in a colloidal state, but in the form of granules too small to be seen even with an ultramicroscope. If, however, it is prepared in the form of a protected colloid in the presence of a suitable proportion of gelatin, these very minute granules unite to form particles large enough to be visible under an ultramicroscope. If this pseudo-solution is submitted in a U-tube to a potential difference of 62 volts, it is sharply concentrated at the side of the positive electrode, the discharge of the particles is complete, and the iodine is obtained in crystalline form. In the presence of a small quantity of sodium thiosulphate the discharge is not complete, and there is simply coagulation. W. G.

The Electrolytic Preparation of Hydroxylamine Hydrochloride. E. P. Schoch and R. H. Pritchett (*J. Amer. Chem. Soc.*, 1916, **38**, 2042—2044).—The method is designed for preparing hydroxylamine hydrochloride on a large scale. The apparatus used is identical with that of Tafel (compare A., 1902, ii, 559), except that the anode used is a lead pipe or rod about 1 inch in diameter instead of the graphite rod used by him. The cathode compartment is filled with a mixture of three volumes of water to one volume of hydrochloric acid (D 1·20). The anode liquid is cooled by causing it to circulate continually through a lead pipe coil immersed in the freezing mixture used to cool the cathode liquid. The current used is 50 amperes at 25 volts, and the nitric acid (D 1·4) mixed with one volume of water is run into the cathode compartment at the rate of 30 c.c. per hour, the addition being allowed to proceed for two and a-half hours. The cathode liquid is concentrated in a vacuum on a water-bath, and the hydroxylamine hydrochloride freed from ammonium chloride by crystallisation from alcohol. W. G.

The "Supposed" Importance of Nitrous Acid in the Formation of Hydrazoic Acid by the Oxidation of Hydrazine. Fritz Sommer (*Zeitsch. anorg. Chem.*, 1916, **96**, 75—80. Compare A., 1914, ii, 266).—A reply to Browne and Overman (A., 1916, ii, 245). The author maintains his view as to the mechanism of the oxidation of hydrazine with the intermediate formation of nitrous acid. C. H. D.

The System Phosphorus in Light of the Theory of Allotropy. A. Smits and S. C. Bokhorst (*Zeitsch. physikal. Chem.*, 1916, **91**, 756—757. Compare A., 1916, ii, 317).—An addendum to the previous paper. It is shown that the sublimation temperature of violet phosphorus is 690·9°. J. F. S.

The Basicity of Hypophosphoric Acid. Ilse Müller (*Zeitsch. anorg. Chem.*, 1916, **96**, 29—63).—In order to determine whether hypophosphoric acid has the single or double formula, the hydrogen-ion concentration in solutions of the salts $Na_2PO_3,5H_2O$ and $NaHPO_3,3H_2O$ has been determined, alizarin-yellow, methyl-red, and *p*-nitrophenol being used as indicators. The salts may be estimated by oxidation with nitric acid, followed by ignition, $NaHPO_3$ being converted into $NaPO_3$ and Na_2PO_3 into $Na_4P_2O_7$. In this way the equilibrium in the system $Na_2O-P_2O_4-H_2O$ has been examined, the following four salts being found to exist at 30°: $Na_2PO_3,5H_2O$, $Na_3H(PO_3)_2,9H_2O$, $NaHPO_3,3H_2O$, and $NaH_3(PO_3)_2,2H_2O$, whilst the two salts $Na_3H_5(PO_3)_4$ and $Na_5H_3(PO_3)_4,20H_2O$ may also have a limited range of existence. These formulæ do not prove that the acid has the double formula $H_4P_2O_6$, as they may possibly be associated compounds of the salts with the acid and with one another. The solubility curves of the first three salts mentioned above have been determined exactly.

Guanidinium hypophosphate (Rosenheim and Pinsker, A., 1910, ii, 708) has the composition $(CH_6N_3)_2PO_3,H_2O$. Sodium molybdohypophosphate (Parravano and Marini, A., 1906, ii, 744) has the composition $Na_2[P(Mo_2O_7)_3],8H_2O$. Hexa-amminocobaltic salts yield a characteristic salt, $[Co(NH_3)_6]NaP_2O_6,3H_2O$, which crystallises from hot concentrated solutions in brown, glistening scales. There is no complete analogy between hypophosphoric and pyrophosphoric acids. C. H. D.

Simultaneous Separation of Two Forms of Silicic Acid from the same Silicate. Gustav Tschermak (*Chem. Zentr.*, 1916, ii, 302; from *Sitzungsber. K. Akad. Wiss. Vienna*, 1916, **125**).—Dilute mineral acids decompose forsterite, Mg_2SiO_4, yielding the sol of orthosilicic acid, whereas the most concentrated acids give a precipitate of metasilicic acid; with mineral acids of medium concentration, the two silicic acids are formed simultaneously. Similar silicates which have so far been investigated (Fe_2SiO_4, $MgCaSiO_4$, Zn_2SiO_4) yielded only the ortho-acid. The atomic volume of forsterite is less than that of the remaining silicates; hence, in addition to the chemical energy, a volume energy is available for the formation of orthosilicic acid from forsterite, which is much greater than that available for the formation of the meta-acid from the same silicate. Lievrite, $FeHFe_2CaSi_2O_9$, resembles forsterite in its behaviour towards acids, and yields both forms of silicic acid when treated with mineral acid of medium concentration. The atomic volume of lievrite is identical with that of forsterite, and, further, a corresponding atomic net can be constructed in which the space relationships of the observed crystal dimensions are analogous. In doubtful cases the behaviour towards dilute acid leads to the recognition of that silicic acid from which the silicate is theoretically derived. H. W.

Concentration of Radium in Carnotite Ores. ALBERT G. LOOMIS and HERMAN SCHLUNDT (*J. Ind. Eng. Chem.*, 1916, **8**, 990—996).—A low-grade American carnotite ore was digested with sulphuric acid at 250—300° for thirty minutes, the mass then treated with a large volume of water, and the insoluble portion subjected to differential sedimentation. Practically all the vanadium and uranium compounds present were dissolved, whilst the fine sands contained 87% of the radium, the concentration of the latter in the sands being from twenty to twenty-eight times more than it was in the ore. A similar separation and concentration of the radium was effected by fusing the ore with sodium hydrogen sulphate or with salt-cake; digestion with sulphurous acid at the ordinary temperature and differential sedimentation of the products yielded a sand containing 85% of the radium at a concentration of ten to twelve times that of the ore. By digesting these concentrates with sulphuric acid, or by fusing them with a mixture of potassium and sodium carbonates, a residue of crude sulphates was obtained containing 80% of the radium at a concentration varying from 150 to 300 times that of the ore. A few experiments were made to ascertain whether treatment of carnotite with chlorine water or carbon dioxide effected a selective extraction of the radium, but the results obtained were not very promising. The radium content of the tailings obtained by treating the ore with sulphuric acid or sodium hydrogen sulphate was estimated by the emanation method and found to exceed the values obtained by comparison of the radiation from equal areas of ore and tailings; it is suggested that, in the latter method, comparisons should be made against standardised tailings instead of ore. W. P. S.

Ammonium Silicate. ROBERT SCHWARZ (*Ber.*, 1916, **49**, 2358—2364).—Evidence of the existence of ammonium silicate is given. The solubility of silicic acid in ammonia solutions depends on the concentration of ammonia, the temperature, and the water content and physical form of the acid. The solubility of the hydrate, $3SiO_2,H_2O$, in $3N$-ammonia at 18° reaches a maximum in about two hundred hours, corresponding with about one-fiftieth of the amount of acid required to form a metasilicate; in $10N$-ammonia at 100° the solubility after one hour reaches 84·3%; in $2N$-ammonia at 100° the hydrate dissolves to the extent of 55·7%, ignited precipitated silica to the extent of 24·4%, both in one hour, whilst finely powdered quartz only loses 2·7% of its weight in a day. Solutions obtained in the hot way have the appearance of colloidal solutions, but the cold preparations are clear. Inasmuch as the conductivity of the ammonia solution rises with time (in the case of the hydrate, with negative acceleration: in the case of the anhydride, with positive acceleration during the first one hundred hours), the formation of a true ammonium silicate seems to be certain.

Although the salt cannot well be isolated, the nearly related *tetraethylammonium silicate*, $(NEt_4)_2SiO_3$, can be obtained as a hygroscopic, amorphous powder by heating the silicic acid hydrate with 10% tetraethylammonium hydroxide in a sealed tube at 80°.

J. C. W.

The Chromates of Silver and the Solid Solutions with Nitrates. FRITZ KÖHLER (*Zeitsch. anorg. Chem.*, 1916, **96**, 207—216).—The properties of silver chromate differ widely with the method of preparation, and contradictory descriptions are therefore found in the literature. In the rhythmical precipitation of silver chromate by means of ammonium dichromate (A., 1916, ii, 554) the small crystals of ammonium nitrate which also separate rhythmically are coloured by silver chromate, being yellowish-green to red, according to the concentration. Similar coloured crystals are obtained when a solution of ammonium nitrate containing a little ammonium dichromate is mixed with a drop of silver nitrate and allowed to evaporate on a glass slide. Exactly similar crystals are obtained when potassium dichromate is used.

Both silver chromate and dichromate can take small quantities of ammonium or potassium nitrate into solid solution. The colour of pure silver chromate is always greenish-black, and the red substance, supposed to be a separate modification, is a mixture of silver chromate and the solid solutions with nitrates.

C. H. D.

Vanadates of Glucinum. PAUL H. M.-P. BRINTON (*J. Amer. Chem. Soc.*, 1916, **38**, 2361—2366).—The author shows that the products obtained by the addition of solutions of soluble vanadates to solutions of glucinum salts are mixtures of variable composition, and not definite salts. The compound glucinum metavanadate, $Be(VO_3)_2,4H_2O$, has been obtained by boiling equimolecular quantities of glucinum hydroxide and vanadium pentoxide with water for about an hour; the solution was filtered and concentrated to about 40 c.c., which usually yielded an orange-red syrup. This, while hot, was poured into a large volume of 95% alcohol, when a copious deposit of yellow particles was produced, which in twenty-four hours had settled to a thick layer of yellow crystals. Viewed under the microscope, these were seen to be yellow, waxy plates. The crystals are isometric, being cubes modified by the octahedron. Glucinum metavanadate is sparingly soluble in cold water, 1 per 1000, but readily so in hot water, and has a strong tendency to supersaturate. It is practically insoluble in chloroform, ether, or absolute alcohol, but is soluble in pyridine to about the same extent as in water. The crystals have D 2·273, and lose the whole of their water of crystallisation over sulphuric acid. J. F. S.

The Atomic Weight of Lead. W. Œchsner de Coninck and Gerard (*Compt. rend.*, 1916, **163**, 514—515).—The lead used was carefully purified by treatment with acids, and from it a sample of pure anhydrous lead nitrate was prepared. A weighed quantity of this was ignited, and the lead oxide left was weighed. The mean value for the atomic weight of lead obtained from four such determinations was 206·98. Using lead obtained from uranium minerals, eliminating as far as possible all lead not of radioactive origin, the value obtained was 206·71. W. G.

Arsenates of Lead. II. Equilibrium in the System, $PbO-As_2O_5-H_2O$. C. C. McDonnell and C. M. Smith (*J. Amer. Chem. Soc.*, 1916, **38**, 2366—2369. Compare A., 1916, ii, 620). The system $PbO-As_2O_5-H_2O$ has been examined by shaking quantities of 2 grams of lead hydrogen orthoarsenate, $PbHAsO_4$, with quantities of 0·0338*N*-ammonia solution (90—180 c.c.) for fourteen hours at 32°. The solutions were filtered and the filtrate analysed. From the results, it is shown that lead orthoarsenate is first produced, the supernatant liquid remaining constant in composition until the conversion is complete, and during this period having the composition $(NH_4)_2HAsO_4$. After the change is complete, solid solutions, varying from lead orthoarsenate to a basic arsenate, are produced, beyond which no change occurs. Lead orthoarsenate was prepared by treating lead hydrogen orthoarsenate with the theoretical amount of *N*/10-ammonia. It is an amorphous powder, D^{15} 7·00. J. F. S.

The Action of Ammonium Monosulphide on Mercuric Sulphide. A. Christensen (*Ber. Deut. pharm. Ges.*, 1916, **26**, 261—266).—Aqueous solutions of ammonium monosulphide when poured on mercuric oxalate, acetate, sulphate, chloride, iodide, or other mercuric salt become yellow in colour, due to the partial liberation of sulphur, with formation of ammonium polysulphide. In confirmation of this explanation, the author adduces the results of an analytical examination of the solution and of the residual solid; the latter is found to consist of a mixture of mercuric sulphide with free mercury. Yellow mercuric oxide, in particular, imparts a yellow colour to ammonium sulphide solution, but the solution gradually loses its colour, because the sulphur slowly returns to the solid matter, with formation of vermilion. Mercuric cyanide when treated with ammonium sulphide solution is comparatively rapidly converted into vermilion, but the solution throughout remains colourless. Mercuric sulphide, already formed, does not yield sulphur to ammonium sulphide solution, so that the liberation of sulphur must occur during the interaction of the mercuric salt and the ammonium sulphide.

Sodium sulphide resembles ammonium sulphide in giving, with mercuric salts, precipitates containing free mercury, although in this case the abnormality is less marked. D. F. T.

Purification and Atomic Weight of Yttrium. B. SMITH HOPKINS and CLARENCE W. BALKE (*J. Amer. Chem. Soc.*, 1916, **38**, 2332—2347).—An historical résumé of the atomic weight determinations of yttrium from 1873 is given. The authors continue the work previously published (A., 1913, ii, 508) on the purification of yttrium salts. They examine in the present paper the chromate method, the ammonia method, and the nitrite method of purification. It is shown that fractional precipitation with potassium chromate is capable of removing considerable quantities of the other rare earths from yttrium, but it will not remove all the erbium or holmium; fractional precipitation with dilute ammonia is tedious and does not produce pure yttria, and fractionation with sodium nitrite is both rapid and effective in freeing yttrium from holmium and erbium. In examining the methods used for the determination of the atomic weight, the authors find that the sulphate synthesis method is not trustworthy, since the value may be made to vary widely by changing the length of time and temperature of ignition. The hydrates $Y_2(SO_4)_3,8H_2O$ and $YCl_3,6H_2O$ are found to be too variable to permit of their use in atomic weight work. The atomic weight of yttrium was determined from the ratio $Y_2O_3:2YCl_3$, using material obtained by means of the above methods of purification, six different fractions being employed. The method was identical with that previously described (*loc. cit.*). As a mean of six determinations, the value $Y=88{\cdot}9$ was obtained, the individual experiments varying between 88·80 and 89·06. J. F. S.

Electrolysis and Purification of Gallium. HORACE S. UHLER and PHILIP E. BROWNING (*Amer. J. Sci.*, 1916, [iv], **42**, 389—398).—An alkaline solution of gallium hydroxide in sodium hydroxide, on electrolysis at the ordinary temperature, usually deposits gallium as liquid globules on the cathode. The authors find that such a solution obtained after the separation of indium (A., 1916, ii, 330) on electrolysis at 0° by a current of 0·28 amp., $D_A=0{\cdot}007$ amp. per sq. cm. and $D_C=6$ amp. per sq. cm., deposits the metal in black, arborescent forms. The deposition of the "gallium tree" depends on the alkalinity of the solution and the curvature of the surface of the liquid globule. A number of photographs of the trees are reproduced in the paper. The trees are hard, like the solid gallium produced in any other manner, and are permanent so long as they are kept at a temperature 10° below the melting point. They are black in colour, although this is chiefly superficial, and when cut present the usual silvery lustre of pure gallium. When placed in water, gas is slowly evolved, and the metal becomes coated with black, grey, and white patches. A separation of gallium and indium may be effected (i) by solution of gallium hydroxide from the mixed hydroxides by sodium hydroxide; (ii) by crystallisation of the ammonium alums from 70% alcohol; and (iii) by crystallisation of the cæsium alums. In the last case it is shown that a gallium preparation containing 10% indium, with traces of zinc, copper, and lead, was practically pure after ten crystallisations. A specimen of electrolytic gallium which contained a trace of zinc was purified by heating the metal in a current of dry hydrogen at a dull red heat, when the whole of the zinc sublimed. A series of photographs of arc spectra of gallium from various purifications is given in the paper, together with a list of wave-lengths. J. F. S.

The Formation of Cobalt Aluminate, Cobalt Orthostannate, and Rinman's Green. J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1916, **96**, 71—74. Compare A., 1915, ii, 636).—The temperature at which cobaltous oxide begins to react with the oxides of aluminium, tin, and zinc varies with the rate at which the mixture has been heated previously, being higher the slower the heating. Dense cobaltous oxide, prepared from the nitrate, gives a higher temperature of reaction than the lighter oxide prepared from the carbonate. For the aluminate, the temperature ranges from 925° to 1025°, but in presence of potassium chloride it may be as low as 776°. The temperature for cobalt and tin oxides is from 1000° to 1075°, not being lowered by potassium chloride. Cobalt and zinc oxides react at 790—800°. C. H. D.

Iso- and Hetero-poly-acids. XIII. The Constitution of the Polymolybdates, Polytungstates and Polyvanadates. ARTHUR ROSENHEIM [and in part MARIANNE PIECK and JACOB PINSKER] (*Zeitsch. anorg. Chem.*, 1916, **96**, 139—181. Compare A., 1916, ii, 334).—The distinction between water of crystallisation and of constitution being difficult, the following method has been found useful. The salt is gently heated in a boat in a stream of carbon dioxide, and the loss of weight determined from time to time, the results being plotted. A series of isotherms may thus be obtained, by a comparison of which the dehydration may be studied and the point at which the compound begins to change in chemical properties observed.

Sodium paramolybdate has the composition

$$5Na_2O,12MoO_3,38H_2O.$$

The guanidinium salt has the composition

$$5(CH_6N_3)_2O,12MoO_3,4H_2O.$$

The following complex paramolybdates have been obtained: $(NH_4)_3H_7[CoMoO_4)_6],5H_2O$, $(NH_4)_4H_6[Cu(MoO_4)_6],5H_2O$, $(NH_4)_3H_7[Mn(MoO_4)_6],3H_2O$,

$(NH_4)_3H_7[Mg(MoO_4)_6],6H_2O$, $(NH_4)_8[Sn(Mo_2O_7)_6],20H_2O$. All these compounds may be regarded as 6-molybdo-aquates,

$$R_5H_5[H_2(MoO_4)_6].$$

There are also numerous polymolybdates belonging to other series.

The alkali paratungstates contain $11H_2O$, but a potassium salt, $2K_2O,5WO_3,4H_2O$, has also been prepared. This may be free from water of crystallisation. The following salts are also described: $5ZnO,12WO_3,35H_2O$, $Na_3H_7[Ni(WO_4)_6],12H_2O$,

$$(NH_4)_3H_7[Ni(WO_4)_6],7{\cdot}5H_2O,$$

cobalt salts of varying composition, and

$$Na_3CuH_5[H_2(WO_4)_6],11{\cdot}5H_2O.$$

These may be regarded as 6-hexatungsto-aquates. A similar conclusion is reached in regard to the polyvanadates. C. H. D.

New Derivatives of Tungsten. J. Bennett Hill (*J. Amer. Chem. Soc.*, 1916, **38**, 2383—2391).—By the action of sodium amalgam on tungsten hexachloride, a compound, $W_6Cl_{12},2HCl,9H_2O$, similar to the molybdenum compound, $Mo_3Cl_6,HCl,4H_2O$ (Rosenheim and Kohn, A., 1910, ii, 300), has been prepared. To prepare this compound, considerable quantities of tungsten hexachloride were required. This was obtained by the action of chlorine on finely divided tungsten in the presence of platinum-black, which is shown to be an extremely good catalyst for this reaction. A mixture of 15 grams of tungsten hexachloride and 105 grams of 3% sodium amalgam was mixed in an ice-cold mortar, placed in a Jena tube, which was closed at one end, and the tube exhausted. The reaction immediately took place, and was very violent. After heating just to redness, and immediately cooling, the contents of the tube were extracted with hydrochloric acid (D 1·08) and filtered, when an intense brown solution was obtained. On extracting this solution with ether, a yellow solution was obtained, which deposited crystals of the above composition. It forms pale yellow, shining needles, which are soluble in alcohol, acetone, acetic acid, and alcohol–ether mixtures, but almost insoluble in anhydrous ether. It dissolved in water, and the solution, on keeping, deposited a yellow compound and then a black compound, both being products of hydrolysis. Potassium hydroxide added to the solution gave a clear yellow solution, which rapidly darkened, and from which weak acids precipitated a black, gelatinous precipitate of hydrated W_2O_3. The brown alkaline solution, on keeping for twenty-four hours in the air, slowly loses its colour, and when treated with weak acids yields a yellow, gelatinous precipitate of hydrated WO_2. J. F. S.

Reduction of Vanadic Acid by Hydriodic Acid. Graham Edgar (*J. Amer. Chem. Soc.*, 1916, **38**, 2369—2377).—Ditz and Bardach (A., 1916, ii, 347) have stated that vanadic acid is reduced by hydriodic acid to vanadium trioxide, according to the equation $V_2O_5 + 4HI = V_2O_3 + 2H_2O + 2I_2$. This conclusion is at variance with the results of many other workers, and in consequence the author has repeated the experiments of Ditz and Bardach in the absence of air. The method adopted consists in placing the requisite amounts of a solution of sodium vanadate, concentrated hydrochloric acid, and a considerable volume of water in a large separating funnel, which is fitted with a second, small separating funnel and a side-tube. A current of hydrogen is passed through the solution for twenty minutes to remove air. Then a quantity of 5% potassium iodide solution is admitted to the mixture, and this is followed by 25 c.c. of carbon disulphide, and the whole mixture shaken from time to time for about an hour. The carbon disulphide solution of iodine is then run off, and a fresh quantity of 25 c.c. of carbon disulphide added, and the process repeated. The addition and removal of carbon disulphide are continued until it becomes impossible to extract any further iodine after several hours' keeping. The combined carbon disulphide solutions are then titrated with sodium thiosulphate solution. From the experimental results, it is seen that the reduction only proceeds to quadrivalent vanadium; further, the reduced vanadium solution is blue in colour, and not green, as it ought to be if the reduction proceeds to the tervalent vanadium derivative. The results of Ditz and Bardach are attributed to oxidation by air of hydriodic acid, and it is shown that this reaction is catalysed by vanadium pentoxide. The mechanism of the reactions between vanadic acid and the halogen hydracids, and the influence of various factors on the equilibrium, has been discussed. J. F. S.

Pure Bismuth. F. MYLIUS and E. GROSCHUFF (*Zeitsch. anorg. Chem.*, 1916, **96**, 237—264).—The estimation of minute quantities of impurities in commercially pure bismuth presents special difficulties, as the oxide and sulphide precipitates, which are amorphous, retain other metals obstinately. The electrolytic method of separation also fails. The basic salts form amorphous precipitates, and the best method of separation is found to be the crystallisation of the normal nitrate from concentrated nitric acid. This is also suitable for the purification of bismuth. The nitrate, if already of fair purity, is dissolved in half its weight of 8% nitric acid and mixed with an equal weight of the concentrated acid. The crystals, which separate on cooling to 0° or $-10°$, are washed with a little ice-cold nitric acid. All impurities are thus concentrated in the mother liquor. The nitrate is converted into oxide by heat, and the oxide is then reduced by fusion with potassium cyanide. A further purification, if necessary, is effected by melting the metal under paraffin and removing the first (purest) crystals by means of a glass spoon.

For the analysis of nominally pure bismuth, 100 grams of the metal are dissolved in nitric acid free from chlorine. A first crop of crystals of nitrate is deposited on cooling, and two further crops may be obtained by evaporating the filtrate. The first and largest crop is redissolved in 8% nitric acid and filtered from tin oxide, if present. Addition of concentrated nitric acid then gives crystals of bismuth nitrate, which may be regarded as pure. The later crops are purified in the same manner, and the united filtrates will yield further crops of colourless crystals, which, however, must be tested for lead, which separates with the crystals as soon as the lead amounts to 1% of the bismuth present.

The insoluble residue contains the tin, antimony, arsenic, gold, silver compounds, silicate slags, and carbon. The final mother liquor contains silver, copper, arsenic, nickel, and other metals. Various samples of bismuth sold as pure contain from 0·03 to 0·25% of impurities, Kahlbaum's bismuth of 1914 containing much less than 0·01%, copper (0·001) being the only impurity present in weighable quantity.

Purified bismuth melts at 271·0°, and when pressed into wire at 195° has a specific electrical resistance of 1·20. C. H. D.

The Action of Oxygen on Ruthenium. A GUTBIER, G. A. LEUCHS, H. WIESSMANN, and O. MAISCH (*Zeitsch. anorg. Chem.*, 1916, **96**, 182—206. Compare Gutbier and Ransohoff, A., 1905, ii, 534).—Finely powdered ruthenium oxidises rapidly when heated in oxygen, the maximum absorption of oxygen corresponding very closely with the formula RuO_2. The value actually obtained is very slightly lower, owing to volatilisation. It is independent of temperature between 700° and 1000°, although the rate of oxidation varies considerably. The formation of the volatile tetroxide begins at 600° and then increases rapidly, being 4000 times as great at 1200° as at 700°. Crystals of the dioxide are observed in the sublimate.

Metallic ruthenium is rendered more compact by heating at 800°. Previous heating at a high temperature in hydrogen reduces the velocity of oxidation. C. H. D.

Analytical Chemistry.

Modification of the Gravimetric Estimation of Chlorine and Silver. ERNST MURMANN (*Chem. Zentr.*, 1916, ii, 427; from *Osterr. Chem. Zeit.*, [ii], **19**, 115).—In the estimation of chlorine and silver the author recommends the reduction of the silver by addition of ash-free paper pulp before or after precipitation. After ignition of the filter and precipitate, the silver remains in the spongy, metallic condition, and can readily be tested for purity. Experiments show it to be free from silver chloride.

H. W.

Direct Estimation of Chlorine in Urine by the Modified Volhard's Method. A. HEIDUSCHKA (*Chem. Zentr.*, 1916, ii, 347; from *Apoth. Zeit.*, 1916, **31**, 279).—Repeated experiments have convinced the author of the necessity of removing proteins before performing the titration. H. W.

Separation of Hydrofluoric Acid and Hydrofluosilicic Acid. J. G. DINWIDDIE (*Amer. J. Sci.*, 1916, [iv], **42**, 421—430).—The author has investigated the various methods which have been suggested for the separation and analysis of a mixture of hydrofluoric acid and hydrofluosilicic acid. The methods due to Katz (A., 1904, ii, 442), Rose, Stolba, and Greef (A., 1913, ii, 975), as well as modifications suggested by the author, all give low values for hydrofluoric acid.
J. F. S.

Reagents for Use in Gas Analysis. V. The Relative Advantages of the Use of Sodium and Potassium Hydroxides in the Preparation of Alkaline Pyrogallol. R. P. ANDERSON (*J. Ind. Eng. Chem.*, 1916, **8**, 999—1001. Compare A., 1916, ii, 262).—Mainly a reply to Shipley (A., 1916, ii, 571). Although the reagent prepared with sodium hydroxide is superior to that prepared with potassium hydroxide as regards specific absorption and cost of materials, it is inferior as regards the time required for complete absorption and the convenience of manipulation.
W. P. S.

Registering Apparatus for the Estimation of Excess of Oxygen in Lead-Chamber Gases. J. B. PÉRÉGRIN (*Ann. Chim. anal.*, 1916, **21**, 223—224).—The apparatus consists of an air-tight chamber of about 30 litres capacity containing a 10-litre varnished caoutchouc balloon filled with hydrogen. This balloon is suspended by a thread attached to a pivoted arm fixed outside the chamber. The gases from the lead chamber are aspirated into the chamber, and any change in the density causes the balloon to rise or fall, the movement being recorded by a registering device (a pen and a moving chart, or a photographic apparatus) connected with the other end of the pivoted arm.
W. P. S.

Titration of Sulphuric Acid. C. R. GYZANDER (*Chem. News*, 1916, **114**, 260—261).—Attention is directed to errors which may be introduced when a sulphuric acid solution is titrated with an alkali solution which has been standardised with an indicator different from that used in the actual titration. A correction should be applied for temperature, when necessary.
W. P. S.

Estimation of Total Nitrogen. Accurate Method of Estimating Ammonia Volumetrically After Destruction of Organic Matter in the Presence of Mercury. ED. JUSTIN-MUELLER (*Chem. Zentr.*, 1916, ii, 520—521; from *Bull. Sci. Pharmacol.*, 1916, **23**, 167—169).—When organic substances are destroyed in the presence of mercury according to Kjeldahl's method, a portion of the ammonia remains combined in the form of mercury ammonium compounds, and is not estimated by the method of Ronchèse. Low results are also obtained after addition of sodium sulphide or hypophosphite, but, according to the author, the results are accurate when potassium arsenite is used to decompose the mercury–ammonium compounds. The estimation is performed in the following manner: urine (10 c.c.) is heated with concentrated sulphuric acid (5 c.c.) and mercury (*ca.* 0·1 gram). If the urine contains sugar the quantity of acid is increased in the ratio of 10% of the sugar content. As soon as the solution becomes colourless, the heating is discontinued, the solution cooled, and diluted to 50 c.c. with water. Five c.c. of the dilute solution are mixed with 10 c.c. of the arsenite solution and 5 drops of phenolphthalein, and neutralised by sodium hydroxide (10%); the precipitate is allowed to settle for a few seconds, filtered, the residue washed three times with water, and the ammonia estimated in the filtrate by the formaldehyde method of Ronchèse. The potassium arsenite solution is prepared by dissolving arsenious oxide (5 grams) with the help of potassium hydroxide (11·20 grams) or *N*-potassium hydroxide (200 c.c.) and making up the solution with water to 1000 c.c. H. W.

The Efficiency of the Aeration Method for Distilling Ammonia; in Answer to certain Criticisms. PHILIP ADOLPH KOBER (*J. Amer. Chem. Soc.*, 1916, **38**, 2568—2572).—Polemical. A reply to Falk (compare A., 1916, i, 439; ii, 341). W. G.

The Boric Acid Method of Estimating Ammonia. LUDWIG ADLER (*Chem. Zentr.*, 1916, ii, 601; from *Zeitsch. ges. Brauwesen*, 1916, **39**, 162—164, 169—172).—The author has investigated the applicability of Winkler's method of estimating ammonia (A., 1913, ii, 527; 1915, ii, 172) in brewers' laboratories. The following precautions ensure good results: 50 c.c. of boric acid solution (40 grams of the crystalline acid in 1000 c.c. of water) are placed in the receiver, and the ammonia is led as deeply as possible into this solution during the first fifteen minutes of the distillation. Evolution of ammonia is complete in twenty minutes. It is necessary to use cooling during the distillation, so that the distillate passes into the receiver at the laboratory temperature. The ammonia is titrated with *N*/4- or *N*/10-sulphuric acid in the presence of methyl-orange. A control solution should be used [water (250 c.c.), a few drops of methyl-orange (0·5%), and *N*/10-sulphuric acid (0·15 c.c.) or the equivalent quantity of *N*/4-acid].

The absorptive capacity of boric acid for ammonia is increased by addition of glycerol. H. W.

Application of the Nitrometer for the Determination of Constitution and Estimation of Nitrogen in a Class of Nitro-compounds (Nitroamines). W. C. COPE and J. BARAB (*J. Amer. Chem. Soc.*, 1916, **38**, 2552—2558).—Using the decomposition flask method of Berl and Jurrissen (compare A., 1910, ii, 240, 242), the nitrometer method can be used for the estimation of nitric nitrogen in nitro-compounds where the nitro-group is attached to carbon through nitrogen. It can also be used for nitroso-compounds of the type of nitrosodiphenylamine, where the nitroso-group is linked to carbon through nitrogen. Other nitroso-compounds of the type of *p*-nitrosodimethylaniline cannot be examined by this method. The nitrates of carbamide and guanidine cannot be estimated in the nitrometer in the usual way. They must first be converted into their respective nitro-compounds, after which they may be readily estimated. W. G.

Estimation of Nitric Nitrogen. F. M. SCALES (*J. Biol. Chem.*, 1916, **27**, 327—337).—The solution containing the nitrate is treated with alumina cream and then boiled with a little magnesia in the presence of a zinc–copper couple. In these circumstances the nitrate is quantitatively converted into ammonia, which distils over into a known volume of standard acid. A simple distilling apparatus suitable for the estimation is described. H. W. B.

Estimation of Amino-nitrogen in Urines containing Dextrose and Albumin. DONALD D. VAN SLYKE (*Proc. Soc. Expt. Biol. Med., New York*, 1916, **13**, 63; from *Physiol. Abstr.*, 1916, **1**, 41).—Albumin is best removed by adsorption on colloidal aluminium hydroxide (Welker); but if much is present it is best to coagulate it first by heat and acetic acid. Urea is removed by urease, but if dextrose is present, it combines with some of the ammonia liberated, and some amino-acid condenses with the dextrose. During urease action, therefore, the urine should be kept acid by adding three or four volumes of water charged with carbon dioxide. Dextrose is then removed by adding copper sulphate; this unites with the sugar and is precipitated by calcium hydroxide. The alkaline filtrate is concentrated in a vacuum; this removes ammonia, and free amino-nitrogen can then be estimated. If albumin is present in diabetic urine this treatment removes the albumin also. G. B.

Use of Uranium in Analyis. J. C. THOMLINSON (*Chem. News*, 1916, **114**, 239).—Potassium ferrocyanide is untrustworthy as an indicator in the estimation of phosphoric acid by titration with uranium acetate solution. W. P. S.

Method of Extraction as Affecting the Estimation of Phosphoric Acid in Soils. HARRISON HALE and W. L. HARTLEY (*J. Ind. Eng. Chem.*, 1916, **8**, 1028—1029).—The authors confirm Brauer's statement (A., 1915, ii, 66) that as much phosphoric acid is extracted from a soil by a two hours' digestion with $2N$-nitric acid as is obtained by a ten hours' digestion with hydrochloric acid (D 1·115); hydrochloric acid also extracts substances from the soil which interfere with the estimation of the phosphoric acid. W. P. S.

Removal of Phosphoric Acid in Qualitative Analysis. LUDWIG GATTERMANN and HANS SCHINDHELM (*Ber.*, 1916, **49**, 2416—2422).—The removal of phosphoric acid by the use of tin was regarded as being due to the formation of stannic phosphate until recent years, when Mecklenburg (A., 1913, ii, 529) advanced the theory that the phosphoric acid was merely adsorbed by the stannic acid, and introduced the idea of using a stannic acid gel instead of metallic tin. Both processes have the disadvantages that the solutions must be as free as possible from hydrochloric acid and that the quantity of tin required is enormous, being about 20 grams of SnO_2 for 0·5 gram of phosphoric acid.

It is now found that a *freshly prepared, cold* solution of crystalline stannic chloride is an excellent agent for removing phosphoric acid, even in hydrochloric acid solutions. Stannic phosphate is precipitated on boiling, in a form which is easily filtered at the pump, the amount of the agent necessary for 0·5 gram being only 2 grams, that is, 1 gram of SnO_2. In a test case, only 0·06% of phosphoric acid was left unprecipitated.

In order to find whether the metals of the ammonium sulphide or carbonate groups are carried down with the precipitate, solutions containing 0·5 gram of phosphoric acid and 5 mg. of the cations were treated with the stannic chloride solution. Chromium and iron are carried down to a certain extent, but all the other metals can be detected with ease in the clear filtrate.

The chief difficulty in applying the method occurs when the amount of phosphoric acid to be removed is small and unknown. An excess of stannic chloride must be used, but if the amount of stannic phosphate is small the stannic acid will not be precipitated in a filterable condition. It becomes necessary then to add phosphoric acid. The following procedure is recommended for the inexperienced worker: starting with 1 gram of substance, the solution from the hydrogen sulphide group is concentrated to 100 c.c., mixed with 5 c.c. of 6% ammonium phosphate, nearly neutralised, acidified with 3 c.c. of 7—8% hydrochloric acid, boiled, and mixed with 3 c.c. of the stannic chloride solution containing one part of the hydrate to one of water. Some of the mixture is filtered and tested with ammonium molybdate, and then the stannic chloride is added 0·5—1 c.c. at a time until succeeding filtrates contain no phosphoric acid. The whole quantity is finally filtered, excess of tin is removed by means of hydrogen sulphide, and the further tests are then proceeded with. The experienced worker is able to judge very largely by the intensity of the molybdate precipitate given by the original substance how much stannic chloride to use. J. C. W.

The Estimation of the Adsorption Capacity of Animal Charcoal. GEORG JOACHIMAGLU (*Biochem. Zeitsch.*, 1916, **77**, 1—13).—A method is given for estimating the adsorption capacity of charcoal by means of iodine solution. A charcoal should have such adsorptive capacity that 0·1 gram takes up at least the iodine equivalent of 10 c.c. of a *N*/10-solution. Those charcoals which have the greatest power of adsorbing iodine also adsorb the largest amounts of methylene-blue and tetanus toxin. When iodine adsorbed on charcoal is administered to the human subject, as much is resorbed in the system as if it had been applied free.

S. B. S.

A New Tube for Soda-Lime. A New Absorbent for Carbon Dioxide in Steel Analysis. G. L. KELLEY (*J. Ind. Eng. Chem.*, 1916, **8**, 1038—1039).—The soda-lime tube described consists of a vertical glass tube 5 inches in height and 1 inch in diameter; it has a neck at the top, and a flat base 1·5 inches in diameter. A capillary inlet is sealed into the side of the tube at a height of 2 inches, the portion of the capillary inside the tube being bent downwards so that it reaches nearly to the bottom of the tube. A layer of cotton-wool is placed at the base of the tube; this is covered with granular calcium chloride, a thin layer of cotton-wool is placed on the latter, and the tube is then filled with soda-lime.

An absorbent, which has about four times the efficiency of soda-lime, is prepared by dissolving 500 grams of sodium hydroxide in 500 c.c. of water, then adding 1000 grams of sodium hydroxide, and stirring in shredded asbestos until the mixture no longer appears capable of wetting more asbestos. The mixture is now heated at 180° for four hours, more asbestos being added gradually, cooled, and ground to pass a 10-mesh sieve. W. P. S.

Separation of Lithium from the other Alkali Metals. SAMUEL PALKIN (*J. Amer. Chem. Soc.*, 1916, **38**, 2326—2332).—The author describes a method for the quantitative separation of lithium from sodium and potassium. Working with about half a gram of the mixed salts, which must be converted into chlorides, the mixture is dissolved in the minimum quantity of water (about 1·5 c.c.), one drop of concentrated hydrochloric acid is added, and then 20 c.c. of absolute alcohol are added drop by drop; this is followed by 60 c.c. of ether (D 0·717). The mixture is left for five minutes and then filtered through a Gooch crucible. The precipitate is well washed with a mixture of 1 part of alcohol and 4—5 of ether. The filtrate is evaporated to dryness, dissolved in 10 c.c. of absolute alcohol, and treated with 50 c.c. of ether and 1 drop of hydrochloric acid, and kept for thirty minutes. It is then filtered through the same Gooch crucible. The filtrate now contains practically nothing but lithium chloride, which is converted into sulphate and weighed in the usual manner. A large number of analyses of mixtures are given, from which it is clear that the method is both rapid and accurate. J. F. S.

Estimation of Manganese in Steel. J. A. CASHMORE (*Chem. News*, 1916, **114**, 239).—Two grams of the sample are dissolved in hydrochloric acid, the solution is treated with a small quantity of potassium chlorate, then evaporated to expel free chlorine, and diluted to about 400 c.c. Zinc oxide suspended in water is now added in excess, the mixture is boiled for two minutes, the precipitate collected on a filter, and washed with hot water. A white precipitate of zinc hydroxide may form in the filtrate, but this is of no importance. The filtrate is heated at 60°, 1 gram of ammonium persulphate and an excess of ammonia are added, the mixture is boiled, and the precipitated hydrated manganese dioxide is collected, washed, ignited, and weighed as Mn_3O_4. It is advisable to dissolve the ignited precipitate in hydrochloric acid and reprecipitate the manganese with ammonium persulphate and ammonia. W. P. S.

The Microchemical Detection of Iron, especially that contained in the "Masked" Form in Plants. ADELE WIENER (*Biochem. Zeitsch.*, 1916, **77**, 27—50).—The method of Macallum (A., 1895, ii, 518) for the setting free of masked iron by alcoholic solutions of mineral acids has been subjected to experimental investigation by the author, who fails to confirm Macallum's statements. Potassium ferrocyanide, when treated with alcoholic solutions of acids in vessels coated with paraffin, failed to give the iron reactions even after ten weeks. It is assumed that in Macallum's experiments the iron found was derived from the glass or the reagents used. In only a very small percentage of cases, furthermore, could iron be detected in plants after hardening the microscopic preparations with acidified alcohol, and attention is directed to the fact that ordinary alcohol of commerce is apt to contain traces of iron. The conclusion is drawn that no really satisfactory method exists for the microchemical detection of masked iron in plants. S. B. S.

Detection of Ferrous Salts in Body Fluids by means of the Phosphotungstic Reagent. ALIN POPESCO (*Chem. Zentr.*, 1916, ii, 427; from *Buletinul Chimie*, 1916, **18**, 3—6).—The author is led to the conclusion that the phosphotungstic reagent (Richaud and Bidot, A., 1909, ii, 350) is not specific for ferrous salts, since the reaction is also shown by other organic and inorganic oxidisable substances. Positive reactions were obtained with stannous chloride, sodium thiosulphate, ammonium sulphide, the alkali sulphides, uric acid, resorcinol, phloroglucinol, ninhydrin, tannin, etc. H. W.

Estimation of Basicity of Chromium Extracts and Infusions. W. APPELIUS and R. SCHMIDT (*Chem. Zentr.*, 1916, ii, 109; from *Collegium*, 1916, 161—164).—The chromium extract or infusion is so diluted that 1—1·5 grams Cr_2O_3 are present per litre. For the estimation of chromium, 50 c.c. of the solution are treated with sodium peroxide, boiled for ten minutes, treated with sulphuric acid, and again boiled for five minutes. The liquid (about 150 c.c.) is transferred to a stoppered flask, 10 c.c. of potassium iodide solution (10%) and 5 c.c. of dilute hydrochloric acid (1 in 4) are added, and, after twenty to thirty minutes, the titration is performed with thiosulphate solution. For the estimation of the copper value (acidity of the acid combined with chromium), 50 c.c. of the diluted solution are boiled for ten to fifteen minutes with copper oxide (0·5—1 gram); the solution is decanted, the residue twice boiled with a small quantity of water, filtered, and washed; the cooled filtrate is treated with 10 c.c. of potassium iodide solution (80:250) and titrated with thiosulphate solution. When the dilute chromium solution is boiled with copper oxide, copper sulphate is formed and chromium precipitated; only about three-quarters of the acid combined with the chromium is transferred to the copper, but the relationship is almost absolutely constant in all cases. A simpler and possibly more accurate process consists in boiling 100 c.c. of the dilute chromium solution with copper oxide (1—2 grams), diluting to 200 c.c., allowing the precipitate to settle, and performing the estimation in 100 c.c. of the clear solution. The copper value is defined as the quantity of copper corresponding with 100 grams of chromium sesquioxide; the relationship between this value and the basicity is expressed in a table.

The process is valid for chromium sulphate, chloride, and formate, but not for the lactate. H. W.

Analysis of certain Tungsten Derivatives. ORLAND R. SWEENEY (*J. Amer. Chem. Soc.*, 1916, **38**, 2377—2383).—A method of analysis of arsenotungstates, antimoniotungstates, and vanadiotungstates is described. In the case of arsenotungstates, a quantity of the sample was placed in a glass tube open at both ends, and this placed in a combustion tube, which was connected with a receiver. The tube was heated at 200°, and a current of dry hydrogen chloride passed over for about an hour. The apparatus was then allowed to cool, the sample moistened with water, and the process repeated for thirty minutes more. This was repeated three times. The receiver was then changed, and the process repeated until the distillate in a fresh receiver contained no arsenic. When the whole of the arsenic had been removed, the contents of the combustion tube were washed into an evaporating dish with dilute ammonia, and evaporated to dryness on a water-bath. The residue was digested with 1:1 nitric acid in the usual way. The residue then consisted of tungsten trioxide and sodium nitrate. This was dissolved in sodium hydroxide, precipitated with mercurous nitrate, and the tungsten weighed as the trioxide. In the case of vanadiotungstates, the same method was employed, but it was found that after a time the material was no longer attacked, although a considerable quantity of vanadium was still present. Consequently, at this point a mixture of chlorine and hydrogen chloride was substituted for the hydrogen chloride, when the whole of the vanadium rapidly distilled over as the reddish-brown oxychloride. The tungsten was estimated as before. The vanadium was estimated by reduction to the vanadyl salt with sulphur dioxide and titration with standard potassium permanganate. The author describes a piece of apparatus in which the separation of the vanadium and tungsten is conveniently carried out. In the case of antimoniotungstates, the same procedure is adopted as in the case of arsenotungstates. Typical analyses in all three cases show that fairly concordant results may be obtained. The author describes two derivatives of bismuthotungstic acid. The sodium, ammonium, and potassium salts of this acid, of the type $3M'_2O,2Bi_2O_3,11WO_3,xH_2O$, were described by Smith and Balke (A., 1904, ii, 179). By treating the potassium salt with a mercurous salt, the author has isolated the compound, $3Hg_2O,2Bi_2O_3,11WO_3,15H_2O$, as a yellow, well-defined, and stable substance. A quantity of this substance was covered with water and a quantity of hydrochloric acid, insufficient completely to decompose it, added. The mixture was kept for several hours and filtered, and the filtrate evaporated at a low temperature under reduced pressure, when a green oil appeared. This was dried in a desiccator over sodium hydroxide until the odour of hydrogen chloride was no longer evident, when a greenish-yellow solid of the formula $2Bi_2O_3,6HCl,11WO_3$ was obtained.

J. F. S.

The Volumetric Estimation of Tin. R. L. Hallett (*J. Soc. Chem. Ind.*, 1916, **35**, 1087—1089).—The methods in common use for the volumetric estimation of tin are critically reviewed, and the means of bringing the tin into a suitable solution discussed.

Stannous chloride solutions may be directly titrated with a solution of ferric chloride in hydrochloric acid; the presence of the chlorides of lead, zinc, aluminium, iron, cobalt, nickel, antimony, copper, and cadmium does not affect the titration except that the presence of a large amount of ferrous chloride retards the finish and lessens the delicacy of the end-point. Bismuth and mercury must be removed. As metallic antimony, copper, and arsenic and tungstic oxide would be precipitated during the reduction of the tin, and would be attacked by hot ferric chloride in acid solution, they must also be removed.

The direct titration of stannous chloride with potassium dichromate or permanganate gives correct results if the tin is completely in the stannous state and no other oxidisable substance is present, but the utility of the method is limited.

The titration of stannous chloride in cold hydrochloric acid solution with standard iodine affords a simple, short, and accurate process for the volumetric estimation of tin. The latter is brought into solution as the chloride and reduced by iron, nickel, aluminium, or antimony. Reduction and titration are best performed in an atmosphere of carbon dioxide in a solution containing not less than 25%, nor more than 40%, by volume of free, concentrated hydrochloric acid; the temperature of the solution to be titrated should not exceed 22°. The sample (0·5 to 2 grams) is brought into hydrochloric acid solution; sufficient concentrated hydrochloric acid is added to make a total of 50 c.c. of concentrated hydrochloric acid, and the solution heated at gentle boiling with a coil of nickel foil for thirty minutes, after any iron which may be present has been reduced. The solution is cooled in an atmosphere of carbon dioxide, the nickel foil removed, and washed with hydrochloric acid (1 in 3). Starch solution is added, and the solution titrated with iodine. Few of the elements ordinarily found in materials to be analysed for tin interfere with this method unless present in so large amount that their colour masks that of the indicator. If antimony is present in quantity of more than 0·1 gram, it will be precipitated in a slimy condition during reduction, but this may be prevented by using a more strongly acid solution (75 c.c. acid instead of 50 c.c.). Copper in quantity of less than 0·05 gram does not interfere, but larger amounts must be removed. Bismuth and tungsten may be disregarded unless present in large amount. Titanium should be removed if present in quantity. Neither bismuth, tungsten, nor titanium in the amounts generally encountered affects the titration, particularly if the latter is performed rapidly; slow and careful titration appears to accelerate their reaction and gives them time to affect the results seriously. An estimation of tin may be accomplished by this method in about one and a-half hours, and the results are accurate to about 0·1%. H. W.

Application of the Method of Constant Boiling Point Mixtures to the Qualitative Analysis of certain Mixed Organic Liquids. W. R. G. Atkins (*Analyst*, 1916, **41**, 334—335).—The identification of a liquid by a determination of its boiling point is possible only when the liquid can be purified previously, and in dealing with small quantities of liquid such purification is frequently a difficult matter. It often happens, however, that another liquid may be added with which the unknown liquid will form a mixture of constant boiling point, so that the latter liquid may be identified in this way; a list of such mixtures, their boiling points, and compositions may be found in Young's "Fractional Distillation," etc. For example, benzene was added to a liquid smelling of alcohol, and the mixture was distilled. The temperature remained constant at 58·35° (the b. p. of the binary mixture of methyl alcohol and benzene) for a short time, thus indicating the presence of methyl alcohol; there were other halts at 64·8°, 68·25°, and 78·3° respectively, these being the boiling points of the mixtures ethyl alcohol–water–benzene, ethyl alcohol–benzene, and ethyl alcohol. The liquid therefore consisted of a mixture of methyl and ethyl alcohols with a trace of water. Other instances are given of the application of the method. W. P. S.

An Accurate Aeration Method for the Estimation of Alcohol in Fermentation Mixtures. Arthur W. Dox and A. R. Lamb (*J. Amer. Chem. Soc.*, 1916, **38**, 2561—2568).—The alcohol solution is saturated with ammonium sulphate, and the alcohol carried over by a current of air at the ordinary temperature into two cylinders of concentrated sulphuric acid, in which it is absorbed. The air is drawn through at the rate of 25 litres per hour, and the aeration is complete in eight to ten hours. The alcohol–sulphuric acid mixture is mixed with 10—15 grams of potassium dichromate in a distillation flask, the cylinders being rinsed with water free from carbon dioxide. The mixture is left for fifteen minutes and then distilled over a free flame, the liquid in the distilling flask being diluted from time to time with water free from carbon dioxide. The results are accurate to within 1·5%. The volatile fatty acids in the original fermented liquid are not carried over in the aeration process. Acetone, although carried over, is not oxidised under the above conditions. Esters, particularly ethyl acetate, interfere with the estimation of alcohol by this method, but they may be determined separately. Aldehydes generally only occur in small quantities in fermentation mixtures, and are not likely to cause any appreciable error. Methyl alcohol under the above conditions is almost completely oxidised to carbon dioxide and water. The presence of toluene does not affect the accuracy of the method. W. G.

Differentation of the Two Naphthols by the Titanic Acid–Sulphuric Acid Reagent. G. Denigès (*Ann. Chim. anal.*, 1916, **21**, 216—217).—An intense green coloration is obtained when a small quantity of α-naphthol is mixed with a solution of titanic acid in concentrated sulphuric acid (compare A., 1916, ii, 544), whilst β-naphthol gives a blood-red coloration with the reagent. If the mixtures are diluted with acetic acid, the green coloration in the case of α-naphthol changes to reddish-violet, but the red coloration given by β-naphthol remains unaltered. If desired, the naphthol may be dissolved previously in acetic acid and the solution poured on the surface of the reagent; under these conditions, α-naphthol gives a green ring at the junction of the two liquids, and a reddish-violet coloured zone appears above the green ring; with β-naphthol, a red-coloured ring develops. These distinctive reactions are also given by the esters of the two naphthols.

W. P. S.

The Colours produced by Resorcinol in Solutions of certain Salts and the Use of these Colours as a means of detecting Resorcinol in the presence of other Phenols. Francis C. Krauskopf and George Ritter (*J. Amer. Chem. Soc.*, 1916, **38**, 2182—2187).—Resorcinol in an ammoniacal solution has been found to give a blue colour with zinc salts (compare Cerdan and de la Puente, *Anal. fis. quim.*, 1913, **2**, 98). Similar colour reactions are given with cobalt salts (violet), nickel salts (bluish-violet), and cadmium salts (blue). Cobalt salts give the most intense colour, and it has been tried to apply this as a test for the presence of resorcinol. The colour is the same in shade and depth whether cobalt chloride, nitrate, or sulphate is used, and it is sufficient to use 1 c.c. of the solution of the cobalt salt, containing 0·4 gram of cobalt per litre, for 50 c.c. of the ammoniacal resorcinol solution. Four c.c. of ammonium hydroxide solution (D 0·90) should be used, and 1 c.c. of a 1% resorcinol solution in 50 c.c. is sufficient to give an intense coloration. The colour takes longer to appear in the absence of air than if air is present, but once formed it is permanent. In contact with air the colour slowly changes to dull green and brownish-black. Under the above conditions the presence of other phenols, such as phenol, pyrogallol, quinol, and catechol, either mask or prevent the formation of the colour due to resorcinol.

By reducing the amount of ammonium hydroxide used to 0·3 c.c. and adding 3 c.c. of alcohol, a deep green colour was obtained with resorcinol, the formation of which was not hindered or masked by the presence of the other phenols. It was possible to detect in 50 c.c. of solution 0·10 gram of resorcinol in the presence of 0·2 gram of quinol or pyrogallol and 0·3 gram of phenol. W. G.

Clinical Methods of Estimation of Sugar in Blood. HARRY RAINY and CHRISTINA M. HAWICK (*Proc. Roy. Soc. Edin.*, 1915–1916, **38**, 186—191).—Bang's micro-chemical method (A., 1913, ii, 446) possesses advantages over several other methods, including those described by Gardner and MacLean (A., 1914, ii, 783), Stein and Wiseley, and MacLean (A., 1916, ii, 613). The quantity of blood required in Bang's method is very small, there is no difficulty about filtration, and the method may also be applied to the estimation of sugar in urine. The authors prefer to soak up the blood on a filter-paper which has been weighed previously in a weighing bottle, and to re-weigh the filter-paper plus blood; an ordinary balance is used in place of the torsion balance mentioned by Bang. Attention is directed to the necessity of boiling all the reagents before use in order to expel dissolved air.

W. P. S.

Estimation of Sugar in Meat Products, particularly Extracts. W. B. SMITH (*J. Ind. Eng. Chem.*, 1916, **8**, 1024—1027).—The removal of proteins, etc., from meat extracts, previous to the estimation of sugar by Fehling's method, is best attained by treatment with picric and phosphotungstic acids, followed by the addition of a minimum quantity of hydrochloric acid. Five grams of meat extract are dissolved in 25 c.c. of water, 4 grams of picric acid and about 50 c.c. of 20% phosphotungstic acid are added, the mixture is diluted to 100 c.c., filtered, 60 c.c. of the filtrate are treated with 3 c.c. of concentrated hydrochloric acid and 3 c.c. of water, again filtered, and the reducing sugars are estimated in this filtrate before and after inversion. W. P. S.

Estimation of Lævulose in Presence of Dextrose. L. LOEWE (*Proc. Soc. Exper. Biol. and Med., New York*, 1916, **13**, 71—72; from *Physiol. Abstr.*, 1916, **1**, 79).—The method depends on the yellow coloration developed after boiling and addition of a 0·2% solution of orcein and a 85% solution of phosphoric acid; the yellow colour becomes orange on addition of alkali. The test is made quantitative by colorimetric comparison with a standard lævulose solution treated with the reagents. Lævulose was detected in 1 c.c. of a 0·05% solution. Sucrose interferes, owing to hydrolysis by the acid. G. B.

Availability of certain Indicators in the Estimation of Gastric Acidity. C. C. FOWLER, OLAF BERGEIM and S. B. HAWK (*Proc. Soc. Expt. Biol. Med., New York*, 1916, **13**, 58; from *Physiol. Abstr.*, 1916, **1**, 40).—A comparative study of certain indicators used in titration of the gastric juice showed that phenolphthalein is most satisfactory for estimating the total acidity, whilst the iodometric method is most useful in estimating the free acidity. Colorimetric determinations of the $H^{\cdot}$ ion concentration are inaccurate when applied to the gastric contents. G. B.

Duclaux's Method for the Estimation of Volatile Fatty Acids. F. W. J. Boekhout and J. J. Ott de Vries (*Centr. Bakt. Par.*, 1916, ii, **46**, 505—513).—The authors have investigated Duclaux's method (A., 1896, ii, 504), and confirm the figures given in his tables for formic, acetic, and propionic acids; in the case of butyric and valeric acids, the results obtained were somewhat different from those recorded by Duclaux. It is shown that if the differences between the quantities of acid found in each successive fraction of the distillate are calculated into percentages of the acid remaining in the flask at the commencement of the distillation of each fraction (this quantity of residual acid being first calculated into 110 c.c. of the solution), a constant number is obtained for each fraction and is the same for each individual acid. This number is 3·5 for formic acid, 5·9 for acetic acid, 11·8 for propionic acid, 19·1 for butyric acid, and 26·0 for valeric acid. The application of the method to the analysis of mixtures of the acids is described. W. P. S.

Estimation of Stearic Acid in Butter Fat. E. B. Holland, J. C. Reed, and J. B. Buckley, jun. (*Chem. Zentr.*, 1916, ii, 350; from *J. Agric. Res.*, 1916, **6**, 101—113).—The experiments were performed according to the method of Hehner and Mitchell, which depends on the fact that when a mixture of fatty acids is dissolved in a solvent saturated at a definite temperature with the acid to be estimated and the solution is then cooled to this temperature, the desired acid is completely precipitated, provided that its solubility is not increased by the presence of other acids. A known weight of mixed fatty acids was warmed with a saturated solution of stearic acid in alcohol (95·25%) until a clear solution was obtained; this was cooled overnight in ice, gently shaken, and, after some time, the mother liquor was decanted as completely as possible. The residue was dissolved in ether, and, after removal of the solvent, dried at 100° and weighed. A series of blank experiments was also performed, since the precipitates retain quantities of mother liquor varying with their weights.

The proportion of stearic acid in the insoluble fatty acids from butter varied from 6·93 to 22·33%, according to the type of fodder and probably also to the individuality and period of lactation. Parallel experiments with beef tallow and palm oil showed a stearic acid content of 30·57% and 31·40% with the former, 8·91% with the latter. H. W.

Modification of Gerhardt's Test for Acetoacetic Acid in Urine. Jacob Rosenbloom (*Biochem. Bull.*, 1916, **5**, 25; from *Physiol. Abstr.*, 1916, **1**, 41).—The test is best carried out as a contact test; 5 c.c. of the urine are poured on top of some 10% ferric chloride solution, and the port-wine colour appears in the zone of contact if acetoacetic acid is present. G. B.

The Estimation of β-Hydroxybutyric Acid in Urine. Erik Ohlsson (*Biochem. Zeitsch.*, 1916, **77**, 232—240).—To 200 c.c. of urine are added 100 grams of ammonium sulphate and 25 c.c. of 20% sulphuric acid. Of the filtrate from this mixture, 275 c.c. are shaken with an equal volume of ethyl acetate in a separating funnel. The ethyl acetate is then transferred to another separating funnel and shaken with 25 c.c. of 30% sodium carbonate solution. The ethyl acetate is then transferred back to the first separating funnel and again shaken with the filtered urine and again transferred to the second funnel and shaken with the solution of sodium carbonate. These processes are repeated five times, and it is found that 93% of the hydroxybutyric acid is thus removed, and this can be estimated polarimetrically in the solution in sodium carbonate. For clinical purposes, a single extraction with ethyl acetate (and subsequent removal of the acid from this solution by sodium carbonate) will suffice. Under these conditions a nearly constant proportion of the hydroxybutyric acid (42%) is removed. S. B. S.

Modification of the Pratt Method for the Estimation of Citric Acid. J. J. Williamson (*J. Amer. Chem. Soc.*, 1916, **38**, 2193—2199).—A critical study of the various steps involved in Pratt's method for the estimation of citric acid (compare U.S.D.A. Bur. Chem., 1912, Circ. 88), as a result of which the author suggests certain modifications by means of which concordant results can be obtained.

In removing the citric acid from a plant juice, the author advises a medium of 30% instead of 50% alcohol (compare Jörgensen, A., 1907, ii, 312). The oxidation should be conducted so that the permanganate solution (0·5 gram per litre) enters at the rate of twenty to twenty-five drops in ten seconds, the distillate passing over at a slightly greater rate. Denigès's solution is added to the distillate at the rate of 15 c.c. for every 100 c.c. of distillate, the precipitate obtained by boiling being estimated volumetrically. The precipitate is dissolved in the least possible quantity of hot 5% hydrochloric acid, the solution cooled, very nearly neutralised with 10% sodium hydroxide solution, and made up to 100 c.c. An aliquot portion of this is poured into an excess of potassium iodide solution (28·0218 grams per litre), and the excess titrated back with a standard mercuric chloride solution. One c.c. of the potassium iodide solution is equivalent to 2·0 mg. of citric acid. W. G.

Detection of Picric Acid in Urine by the *iso*Purpurate Reaction. Ydrac (*Ann. Chim. anal.*, 1916, **21**, 225; from *Union Pharm.*, 1916, 337).—This reaction gives the most trustworthy results when carried out as follows. The urine is rendered slightly alkaline to litmus paper by the addition of a few drops of *N*/10-sodium hydroxide solution, potassium cyanide solution is then added, and the mixture heated at 60° to 70°; if picric acid is present, a red coloration develops after a few minutes. The test will detect the presence of as little as 0·025 gram of picric acid per litre of urine. Icteric urine does not give a coloration with the test, and albumin and biliary pigments do not interfere.

W. P. S.

Estimation of Hippuric Acid in Urine, Blood, Muscles, and Liver. HIIZU ITO (*J. Amer. Chem. Soc.*, 1916, **38**, 2188—2192).—The hippuric acid was converted into benzoic acid by boiling it with 25% sodium hydroxide for twelve hours, the solution then being acidified and extracted with light petroleum in a modified Soxhlet apparatus for extracting liquids, the petroleum being evaporated from the weighed extraction flask by a current of dry air, and the benzoic acid weighed. In the case of urine, any benzoic acid present was first removed by extraction before the hydrolysis. In the case of blood, it was defibrinated, and the protein and fat separated by heating it on a water-bath with dilute hydrochloric acid. In the case of muscle and liver, the material was finely shredded and extracted with hot water, the protein and fat removed as above from the filtrate, the filtrate being finally evaporated nearly to dryness and extracted with alcohol. After this treatment, the residue was hydrolysed and the estimation performed as above. W. G.

Colour Reactions of Aromatic Aldehydes. PETER POOTH (*Chem. Zentr.*, 1916, ii, 522; from *Schweiz. Apoth. Zeit.*, 1916, **54**, 377—382. Compare Häuszler, *Zeitsch. anal. Chem.*, 1913, **53**, 363, 691).—The condensation of aromatic aldehydes with sulphonated aromatic amino-compounds leads to the formation of characteristic, distinctly coloured azomethines, which can be employed in the identification of aldehydes. Aromatic aldehydes yield more distinct colorations with naphthionic than with sulphanilic acid; in most cases, the azomethine separates directly on cooling. The test is performed as follows: 3—4 c.c. of an aqueous solution of sodium sulphanilate or naphthionate (10%) are heated in a porcelain dish on the boiling-water bath; a boiling alcoholic solution of the aldehyde is added, which causes the appearance of a pale yellow to red coloration, and the solution is evaporated to dryness, the colour generally being deepened thereby. Before evaporation, a few drops of the solution are removed, diluted with water, cooled, and treated with a few drops of dilute sulphuric acid; in many cases the colour is deepened, in others completely changed. Certain of the reaction products, particularly those derived from nitro-aldehydes, are sensitive to daylight. The products obtained from substituted aldehydes are less stable.

The colorations given by the individual aldehydes are described and tabulated in the original paper. H. W.

Estimation of Vanillin in Vanilla Extract. Arthur W. Dox and G. P. Plaisance (*Amer. J. Pharm.*, 1916, **88**, 481—484).—Thiobarbituric acid may be used for the quantitative precipitation of vanillin. To estimate vanillin in vanilla extract, 25 c.c. of the sample are heated to expel alcohol, and then diluted to 50 c.c. with lead acetate solution. After a few hours, the mixture is filtered, 40 c.c. of the filtrate are treated with hydrochloric acid in quantity sufficient to make the acidity 12% and the volume 50 c.c., the lead chloride is separated by filtration, and 40 c.c. of this filtrate are mixed with thiobarbituric acid in 12% hydrochloric acid solution. The precipitate, which is the simple condensation product, 4-hydroxy-3-methoxybenzylidenemalonylthiocarbamide, is collected after eighteen hours, washed with 12% hydrochloric acid, then with water, dried at 98°, and weighed. Thiobarbituric acid is a general precipitant for aromatic aldehydes, and the method cannot be applied to artificial extracts which have been coloured with caramel, since the latter contains furfuraldehyde derivatives. The presence of caramel in an extract is indicated by the brown precipitate which forms when phloroglucinol is added to the clarified extract containing 12% of hydrochloric acid. W. P. S.

A Comparison of Barbituric Acid, Thiobarbituric Acid, and Malonylguanidine as Quantitative Precipitants for Furfuraldehyde. Arthur W. Dox and G. P. Plaisance (*J. Amer. Chem. Soc.*, 1916, **38**, 2156—2164).—Of the three reagents tested, barbituric acid only gives a quantitative precipitation with furfuraldehyde in solution in 12% hydrochloric acid when a large excess (eight to sixteen times the theoretical quantity) of the barbituric acid is used (compare Unger and Jäger, A., 1903, ii, 187, 456). Thiobarbituric acid, on the other hand, gives a quantitative precipitation without any large excess being used, the results being, if anything, slightly too high. The reaction is quantitative for such small amounts of furfuraldehyde as 12 mg. This reagent is preferable to phloroglucinol, since no correction for solubility of the precipitate is necessary. Furthermore, the precipitate is a definite compound, *furfurylidenemalonylthiocarbamide*, which is bright lemon-yellow in colour, very flocculent, and voluminous. It is easy to filter and wash. The thiobarbituric acid used must be quite pure and free from any cyanoacetic ester, or the results obtained will be too low. Like phloroglucinol, it also gives a precipitate with methylfurfuraldehyde.

The condensation of furfuraldehyde with malonylguanidine is not quantitative. W. G.

Estimation of Salol and Acetanilide in a Mixture of the two, and of Salol and Phenacetin in their Mixtures. Benedict Salkover (*Amer. J. Pharm.*, 1916, **88**, 484—485).—A method for the estimation of these substances when in the form of tablets and mixed with talc, starch, acacia, tragacanth, etc., depends on the insolubility of acetanilide and phenacetin in light petroleum, and on the solubility of salol in this solvent. A weighed portion of the powdered tablets is shaken for thirty minutes in a closed flask with a measured quantity of chloroform; an aliquot portion of the chloroform solution is then filtered into a weighed flask, the chloroform is evaporated, the residue is dried at 60°, and weighed. It represents the salol and acetanilide, or salol and phenacetin, contained in the mixture. Another portion of the sample is now extracted in a similar way with light petroleum. The residue obtained when an aliquot portion of the solution is evaporated consists of salol, but its weight must be corrected for a small amount of acetanilide or phenacetin which is dissolved. One hundred c.c. of light petroleum (b. p. 40—45°) dissolve 0·015 gram of phenacetin or 0·022 gram of acetanilide.

W. P. S.

Bromine and Iodine Compounds of Hexamethylenetetramine (Urotropine). K. Sugiura and K. G. Falk (*Biochem. Bull.*, 1916, **5**, 17—21; from *Physiol. Abstr.*, 1916, **1**, 65).—A method of estimation of this extensively used drug can be based on the formation of the tetraiodide. G. B.

Estimation of Polypeptides and Amino-acids in Blood. J. Amann (*Chem. Zentr.*, 1916, ii, 430—431; from *Schweiz. Apoth. Zeit.*, 1916, **54**, 309—313).—The following method is adapted for clinical purposes. Fresh, centrifuged blood serum (1 c.c.) is placed in a suitable dialyser which has been shown to be impermeable to albumin, but readily permeable to polypeptides, and, after addition of a few drops of toluene, dialysed for sixteen hours at 37° against sterilised water (10 c.c.) saturated with toluene. Five c.c. of the dialysed solution are mixed with ninhydrin solution (1%, 0·2 c.c.); on the other hand, 1 c.c. of a solution prepared by hydrolysing casein with sulphuric acid (25%) and containing 10 mg. N in 100 c.c., is diluted with water (4 c.c.) saturated with toluene, and ninhydrin solution (0·2 c.c.) is added. The two solutions are placed in the boiling-water bath for twenty minutes, cooled, and their colorations compared in the chromometer. With similar intensities, the concentration of amino-nitrogen is inversely proportional to the thickness of the layer. In the place of the standard solution described above, solutions of mixtures of methyl-violet, methylene-blue, and aniline-brown can be employed. When approximate values only are required, the chromometer can be dispensed with. H. W.

General Conceptions of Intoxication. II. Protection against "Structure" Poisons; a Method for Biochemical Detection of small amounts of Substances. Martin Jacoby (*Biochem. Zeitsch.*, 1916, **76**, 321—325. Compare A., 1916, i, 778).—Hæmolysis (or agglutination) of red blood corpuscles by mercuric chloride or copper sulphate can be prevented by the addition of the requisite amount of potassium cyanide. As only very small amounts of the reacting substances are employed, it is suggested that these facts form a basis of a biochemical method for estimating small amounts of the cyanide. S. B. S.

The Content in Suprarenin [Adrenaline] in the Ordinary Commercial Preparations and the Methods of Estimation. FRITZ JOHANNESSOHN (*Biochem. Zeitsch.*, 1916, **76**, 377—391).—Adrenaline can be estimated colorimetrically by Folin's phosphotungstic reagent, and biologically by the perfusion method of Läwen and Trendelenburg when present by itself, but not in the presence of novocaine or alypin. When these substances are present, however, the colorimetric method of Fränkel, Allers, and Bayer can be used (iodic acid in the presence of sulphanilic acid) under conditions specified by the author. This method has been employed for estimating the adrenaline content of various commercial preparations and of the conditions under which these may be preserved without loss of the adrenaline. S. B. S.

Palpitation and Caffeine; Detection of Caffeine in Urine. A. CH. HOLLANDE and L. THÉVENON (*J. Pharm. Chim.*, 1916, [vii], **14**, 324—326).—Malingerers sometimes take a dose of 1 gram or more of caffeine before undergoing a medical examination, since this alkaloid increases the heart-beats up to 160 per minute. When such large doses are taken, caffeine is easily detected in the urine; the authors have isolated 0·26 gram of caffeine from 2 litres of urine passed by a man who had taken 1 gram of the alkaloid. In suspected cases the urine should be treated with 10% of its volume of basic lead acetate solution, filtered, the filtrate treated with sodium sulphate to precipitate excess of lead, and the solution then extracted with chloroform. A distinct, crystalline residue is obtained on evaporating the chloroform extract if caffeine is present, and the latter may be identified by the usual reactions. In the absence of caffeine, an amorphous residue remains when the chloroform solution is evaporated.
W. P. S.

A New Method for the Estimation of Nicotine in Tobacco. ALFRED TINGLE and ALLAN A. FERGUSON (*Trans. Roy. Soc. Canada*, 1916, [iii], **10**, 27—31).—Based on results already given (A., 1916, i, 656), the authors have worked out a new method for the estimation of nicotine in tobacco. Into a 500 c.c. flask they place 20 grams of tobacco, 40 grams of barium hydroxide, and 150 c.c. of water, and distil the mixture with steam until the distillate gives no alkaline reaction with phenolphthalein. To the distillate 20 c.c. of sulphuric acid are added, and the liquid evaporated to about 50 c.c. This solution is made strongly alkaline with potassium hydroxide, a few drops of baryta water being added for clarification. The solution is then made up to 100 c.c., the precipitate allowed to settle, the supernatant liquid filtered, and its rotation then determined in the polarimeter. In a modification of the method, the nicotine is extracted from the steam distillate by chloroform. These two methods gave concordant results, which were then compared with the results obtained, using the same specimen of tobacco, by the methods of Tóth and of Kissling. The latter processes give lower results than were obtained by the methods of the authors. T. S. PA.

Estimation of Strychnine in Nux Vomica. H. R. JENSEN (*Pharm. J.*, 1916, **97**, 458—461).—The hot (50°) nitration method prescribed in the British Pharmacopœia for the separation of strychnine from brucine yields low results; the deficiency in the amount of strychnine found may be from 5 to 11% of the quantity present. Nitration at 20° is recommended, provided that the nitric acid used is "active" or is "activated" by the addition of sodium nitrite. Attention is called to the fact that strychnine nitrate in an aqueous solution containing sulphuric and nitric acids is not readily decomposed when the solution is rendered alkaline; small quantities of strychnine nitrate are "salted out," and are extracted by the chloroform. The residue of alkaloid obtained when the solvent is evaporated should be weighed and then titrated; the difference between the two results indicates the quantity of strychnine nitrate present (the average quantity is 8·8% of the weight of the residue), and the true amount of alkaloid is obtained after applying this correction. W. P. S.

Chemical and Physiological Detection of several Alkaloids in the same Solution. EDUARDO PHILIPPI (*Chem. Zentr.*, 1916, ii, 604—605; from *Arch. Farmacol. sperim.*, 1916, **22**, 120—130).—The characteristic reaction of strychnine with sulphuric acid and potassium dichromate is not shown by 1 mg. of strychnine nitrate in the presence of 0·04 gram or more of quinine bisulphate, a transitory, garnet-red coloration being produced, which becomes green or greenish-grey; with smaller quantities of quinine, the reaction is distinct, but transient. The same effect is observed when salts of the alkaloids with the same acid or the free alkaloids are used. Crystals of strychnine picrate can be obtained in the presence of a large excess of quinine, but they are not then characteristic. The alkaloids are most simply and certainly separated by the use of sodium potassium tartrate; quinine tartrate is insoluble in solutions of alkali sulphates and tartrates, whereas the strychnine salt is soluble. Mixtures which do not give the characteristic reaction with potassium dichromate do not cause the characteristic symptoms in the frog. This effect is probably not due to delayed absorption, but rather to a superposition of the symptoms of poisoning in which those predominate which are attributable to the alkaloid present in excess. H. W.

Volumetric Estimation of Indigotin. SAMUEL M. JONES and WALTER SPAANS (*J. Ind. Eng. Chem.*, 1916, **8**, 1001—1002).—The indigotin is sulphonated and then titrated with formaldehyde-sodium sulphoxylate. One gram of the powdered indigo (or 5 grams of a 20% paste) is heated at 60° for four hours with 30 c.c. of sulphuric acid (D 1·84); the mixture is then cooled, diluted with water, again cooled, diluted to 1 litre, and filtered. Fifty c.c. of the filtrate are placed in a flask, 50 c.c. of 35% sodium hydrogen sulphite solution are added, a current of hydrogen is passed into the flask, the contents of the latter are heated at 75°, and titrated at this temperature with a 0·1% formaldehyde–sodium sulphoxylate solution. The flask should be closed with a cork through which pass inlet and outlet tubes for the hydrogen, a thermometer, and the nose of the burette. The formaldehyde–sodium sulphoxylate solution is standardised against pure indigotin under the conditions mentioned. W. P. S.

Indoxyl in Urine. ED. JUSTIN-MUELLER (*Chem. Zentr.*, 1916, ii, 242—243; from *Bull. Sci. Pharmacol.*, 1916, **23**, 85—92).—Maillard's hypothesis, according to which indigotin and indirubin are formed by polymerisation of hemi-indigotin pre-formed in urine, is criticised.

The following method is recommended for the detection of indoxyl in urine. About 10 c.c. of urine are treated with an equal volume of pure hydrochloric acid or half the volume of pure sulphuric acid; the solution is cooled and shaken with ether (2—3 c.c.). If the ethereal layer is not coloured, 2 to 4 drops of hydrogen peroxide (10%) are added, and the solution is again shaken, 2—3 drops of alcohol being added if an emulsion is formed. Addition of hydrogen peroxide is unnecessary if the characteristic coloration of the ether is produced by addition of the acid alone. In the presence of iodides and absence of indoxyl, the ether becomes yellow; if both are present, a green coloration is formed. Methylene-blue is not dissolved by ether.

Indoxyl is estimated in urine in the following manner: 50 c.c. of urine are purified by addition of lead acetate (4 c.c.) and so much crystalline sodium sulphate that the total volume is 55 c.c.; 11 c.c. of the filtered solution (=10 c.c. of the original urine) are mixed with pure hydrochloric acid (10 c.c.) and, if necessary, 2—5 drops of hydrogen peroxide (10 %). After being cooled, the solution is shaken with chloroform (3—5 c.c.), the chloroform layer removed, and the extraction repeated two or three times with such quantities of solvent that the total volume of the latter amounts to 9—10 c.c. The volume of the chloroform extract is made up to exactly 10 c.c., and the colour of the solution compared with that of a standard prepared by dissolving indigocarmine (0·89 gram) in boiling water (200—250 c.c.), addition of phenol (1 gram) to the filtered solution, and dilution to 500 c.c. It should be noted that the extracts have a rather more pronounced violet shade than the standard solutions.

Indigotin is formed by the condensation of two molecules of indoxyl, indirubin by the oxidation of indoxyl (1 mol.) to isatin, and condensation of the latter with one molecule of indoxyl. Indigotin and indirubin are thus both directly formed from the indoxyl in urine. Maillard's hypothesis of the existence of pre-formed indigotin may therefore be abandoned, as well as the supposition of the existence of two polymeric indigotins. H. W.

Microchemistry of Plants. XIV. Identification of Crocetin. O. TUNMANN (*Chem. Zentr.*, 1916, ii, 279; from *Apoth. Zeit.*, **31**, 237—238).—The investigation was undertaken with the object of discovering reactions by which crocetin can be distinguished from other carotinoids, particularly from carotin, and for this purpose powdered saffron was employed.

Coniine-crocetin, obtained by spreading the powder on a drop of water, addition of 1% coniine solution, and warming, is suitable for identification of crocetin. During drying, deep yellow, single, prismatic needles with direct extinction are formed. The microchemical preparations of the sodium and potassium compounds of crocetin cannot be accomplished by Decker's macrochemical method. The former is best obtained by boiling saffron powder for three to five minutes with 10% sodium carbonate solution; during drying, pale yellow nodules are formed, which become crystalline in a few days, the process being accelerated by addition of alcohol. The potassium compound is obtained by warming saffron powder with water and addition of alcoholic potassium hydroxide solution; a copper-red precipitate, consisting of fine drops, is first produced, which becomes powdery in the course of a few days, but never yields crystals. In addition, chrome-yellow, oily masses are formed, which within one to two hours become crystalline. The copper-red drops consist of carotin, the yellow crystals of potassium crocetin. The latter is readily soluble in water, which scarcely affects the carotin. Red drops only are formed in the pollen grains.

When the red solution of crocetin in dilute pyridine (1:1) is dried, reddish-brown, interlaced rhombs are produced, and crystallisation occurs in the course of a few days. The preparation of aniline-crocetin is readily accomplished, and forms the best method of identifying crocetin. Saffron powder is warmed for two to three minutes with aniline until bubbles commence to form; in the course of ten to twelve hours, numerous dark red nodules are formed, which dissolve slowly in alcohol and glycerol. If saffron powder is warmed with very dilute sodium hydroxide solution, treated with benzoyl chloride, and warmed until bubbles commence to form, fine, pale yellow and golden-yellow needles, grouped in tufts and clusters, are produced. H. W.

A Direct and Indirect Diazo-reaction for Bilirubin. A. A. HYMANS VAN DEN BERGH and P. MULLER (*Biochem. Zeitsch.*, 1916, **77**, 90—103).—The ordinary diazonium reaction for bilirubin as originally devised by Ehrlich was carried out in the presence of alcohol. It has been found by the authors that human bile yields the diazonium reaction in the absence of alcohol, and this they designate the "direct" reaction, in contradistinction to the "indirect" action, which is generally given by bilirubin in the presence of alcohol. They find that bilirubin ordinarily gives a colour with diazonium solutions in the presence of (1) methyl or ethyl alcohol; (2) salts of weak acids, such as cholic and citric acids; (3) when a trace of alkali has been added to the bilirubin solution. They have failed to discover what substance is present in human bile which causes the "direct" action, that is, the colour reaction with diazonium solutions without addition of alcohol or the other substances mentioned above. They have applied the diazo-reaction to various sera, and find that horse-serum, which normally contains bilirubin, yields only the indirect action, as do also sera in which the presence of bilirubin is due to hæmolytic processes; on the other hand, sera of patients with jaundice due to obstruction give, at any rate in certain stages of the disease, a direct diazo-reaction. S. B. S.

Microchemistry of Æsculin and its Detection in Æsculus hippocastanum. O. Tunmann (*Chem. Zentr.*, 1916, i, 1277—1278; from *Schweiz. Woch. Chem. Pharm.*, **54**, 45—47, 67—70).—Æsculin prepared from the bark of thin branches (thumb-thick) of *Æsculus hippocastanum* gathered in October crystallises from alcohol in large and small, flat prisms, m. p. 161°, the stellate or radiating groups of needles mentioned in the literature not being obtained.

For microchemical purposes the most suitable solvents are methyl alcohol and pyridine; from the latter æsculin separates in arborescent masses of needles. Dissolution of a crystal of æsculin in warm chlorine water is rapidly followed by the separation of a chloro-compound in shrub-like aggregates of filamentous, strongly polarising needles, which appear pale yellow in a thick layer. Dibromoæsculin, obtained by treating a saturated aqueous æsculin solution with potassium bromide solution containing 10% of dissolved bromine, separates as a flocculent precipitate, rapidly becoming crystalline. Gold chloride dissolves when heated in æsculin solution and gives rise after a short time to a deep blue, granular, crystalline precipitate. In sections, æsculin is best detected by means of the dibromo-derivative; the sections are left under a cover-glass in the reagent for some hours and are then cleared with aniline. T. H. P.

Detection of Ovalbumin in Urine. P. Godfrin (*J. Pharm. Chim.*, 1916, [vii], **14**, 257—260).—Twenty-five c.c. of the urine are treated with 5 drops of glacial acetic acid and excess of sodium chloride; this treatment precipitates ordinary albumin, but not ovalbumin. After thirty minutes the mixture is filtered and the filtrate tested for the presence of ovalbumin, for which purpose Tanret's reagent is recommended. If the urine contains pseudo-albumins, the sodium chloride should be added thirty minutes after the addition of the acetic acid, and a further thirty minutes allowed to elapse before the mixture is filtered. W. P. S.

Criticism of the Method of Detecting Urinary Albumin by Heat; New Process permitting the Detection of the smallest traces of Albumin in Urine. P. Godfrin (*J. Pharm. Chim.*, 1916, [vii], **14**, 294—303).—The author considers that by the usual method of acidifying the urine with acetic acid and saturating it with sodium chloride or sodium sulphate, an error may arise due to the precipitation of pseudo-albumin. He recommends the following procedure. The reagent is a mixture of 90 c.c. of a cold saturated solution of sodium chloride and 10 c.c. of phosphoric acid (50%), the mixture being filtered. To 9 c.c. of the urine, acidified if necessary with dilute acetic acid and filtered, 1 c.c. of phosphoric acid (50%) is added, and the mixture filtered if necessary. Three to four c.c. of the filtrate are carefully run on to an equal volume of the above reagent, and the tube left for a time. The amount of albumin in the urine is indicated by the time taken for the formation of an opaque disk at the junction of the liquids, and also by the opacity of the ring. At the most, half an hour is sufficient for the formation of a nebulous ring indicative of the smallest traces of albumin in the urine. If uric acid separates during the test, it can be redissolved by plunging the test-tube into water at 50°, without mixing the layers. This method only precipitates albumin and primary albumoses, and the precipitate due to the latter disappears if the tube is plunged into water at 60°. W. G.

Rennin. Howard T. Graber (*J. Ind. Eng. Chem.*, 1916, **8**, 909—910. Compare A., 1912, ii, 706).—There appears to be a seasonal variation in the rate at which milk is coagulated by rennin, the coagulation being more rapid, by some minutes, in the autumn and spring than in the summer and winter. In a method described previously for the assay of rennin (*loc. cit.*) the quantity of milk specified for use in the test was twice the volume intended. The corrected method is as follows: 0·4843 gram of the rennin is dissolved in 150 c.c. of water, and 10 c.c. of this solution are added to 1 quart of milk at 42°; the mixture is poured from one vessel to another three times and the time then observed when coagulation commences. Ten c.c. of the rennin solution with 1 quart of milk gives a proportion of 1:30,000, and the activity of the rennin used is reported as being 1:30,000 in the time required for the coagulation. W. P. S.

A Résumé of Tests for Pepsin. Howard T. Graber (*J. Ind. Eng. Chem.*, 1916, **8**, 911. Compare A., 1912, ii, 706).—The albumin used in testing the strength of pepsin should be obtained from eggs which are from five to twelve days old, since with these eggs the amount of insoluble residue left after treatment with an active pepsin rarely exceeds 1 c.c. in volume. The volume of the residue also affords an indication of the age of the eggs used; a larger insoluble residue than usual shows that the eggs are quite fresh or more than twelve days old. If a second test after six days gives a smaller residue, the eggs were fresh, whilst an increased quantity of residue shows that the eggs were more than twelve days old. W. P. S.

General and Physical Chemistry.

The Spectra of Carbon and Hydrocarbon. CHARLES W. RAFFETY (*Phil. Mag.*, 1916, [vi], **32**, 546—559).—Photographs of the "Swan" spectrum obtained under varying conditions are discussed in detail. A new series of faint lines in the region of λ 4107—λ 4025 is described, together with some bands of unknown origin which are associated with the "Swan" spectrum.

H. M. D.

Regularities in the Spectra of Neon and Argon. K. W. MEISSNER (*Physikal. Zeitsch.*, 1916, **17**, 549—552).—Recent measurements of the wave-lengths of lines in the red portion of the neon spectrum show that all the more intense lines are members of groups of triplets or quadruplets characterised by the same wave-number differences. Similar quadruplets are found in the red region of the argon spectrum, but the groups are in many cases incomplete.

H. M. D.

The Groups of Rays of Iron under the Selective Influence of Thermal and Chemical Actions. G. A. HEMSALECH (*Compt. rend.*, 1916, **163**, 757—759. Compare A., 1908, ii, 445).—The iron rays emitted by a Bunsen flame may be divided into three classes, namely: (1) Rays emitted by the exterior flame and strengthened in flames of higher temperature, being particularly sensitive to thermal actions. Examples are λ 3860, 3920, 4376. (2) Those rays emitted under the influence of chemical action; they are very marked in the cone but feeble in the flame. Examples are the triplets at λ 4046 and 4384. (3) This class includes the rays of the "supplementary" spectrum, that is, the rays of the cone proper. Examples, λ 3936, 4119, 4957. In each of these categories of spectra there are peculiar groups of rays, composed of three, four, or more rays. The groups of the first and second class converge towards the red and of the third class towards the violet.

W. G.

Optical Investigations of the Constitution of Nitric Acid. KONR. SCHAEFER [with H. NIGGEMANN] (*Zeitsch. anorg. Chem.*, 1916, **97**, 285—311. Compare A., 1910, ii, 562).—Optically pure nitric acid up to 12*N* may be obtained by distilling the ordinary pure acid, D 1·4, over carbamide. More concentrated acid is obtained by distilling the ordinary acid, mixed with two or three volumes of sulphuric acid, in a vacuum apparatus consisting entirely of glass and protected from light.

The solutions are contained in vertical absorption vessels provided with plane parallel plates of silica, the inner tube being raised or lowered to vary the thickness of the absorbing layer. For high temperatures, the vessel is surrounded by an electrically heated copper block, and for low temperatures by a cooling coil and vacuum jacket.

Soluble nitrates exhibit selective absorption, whilst alkyl nitrates only cut off the ultra-violet end of the spectrum. Dilute nitric acid, from 0·02 to 1*N*, has a spectrum like that of the salts, but at 2*N* a transition to the ester type begins, and the concentrated acid has only continuous absorption. Solid and molten potassium nitrate have an absorption band in the same position as the solution. The difference between the two types of spectra is not attributable either to dissociation or to hydration, and can only be explained by a difference in the arrangement of the subsidiary valencies in the NO_3 group. C. H. D.

The Ultra-violet Absorption Spectra of Blood Sera. S. Judd Lewis (*Proc. Roy. Soc.*, 1916, [B], **89**, 327—335).—Quantitative measurements of the ultra-violet absorption of blood sera have been made by the use of a sector spectrophotometer in conjunction with a quartz spectrograph. The intensity of the absorption was determined by matching the absorption spectrum against normal spectra of known intensity, and the results are shown by a curve in which the extinction-coefficient is plotted against the wave-length of the ultra-violet radiation.

The absorption curve for normal serum shows a well-marked band with a maximum at about λ 2800, followed by a minimum at λ 2540, from which point the absorption curve rises steeply to a second maximum at about λ 2400. From a comparison of the curves for a large number of samples of normal serum, it appears that the section of the curve between the maximum at λ 2800 and the minimum at λ 2540 is the portion which is most subject to variation. The examination of pathological sera has also shown that this section of the curve is the region where the greatest differences are to be found. There is, moreover, distinct evidence in favour of the view that the minimum at λ 2540 is displaced appreciably under certain pathological conditions.

Since serum is a mixture of substances in somewhat variable proportions, the absorption curves represent the resultant of several superposed curves, each characteristic of some constituent of the serum. By separating the proteins from the non-proteins and comparing the spectra of the corresponding solutions, it has been found that the chief central band (maximum at λ 2800) is due almost entirely to proteins.

Some observations on horse serum and egg-albumin show that the absorption curves are of similar kind. In the case of horse serum, the minimum is at λ 2510 instead of λ 2540, and the curve for the protein band is of rather larger dimensions than the corresponding curve for human serum. The protein band of egg albumin is, on the other hand, more symmetrical in form, but the minimum absorption is at the same wave-length (λ 2540).

H. M. D.

The Chromophore Function. I. Lifschitz (*Zeitsch. wiss. Photochem.*, 1916, **16**, 101—110).—A general statement of the author's views on the nature of chromophoric groups and their selective absorption effects. H. M. D.

Influence of Light on the Loss of Water of Crystallisation from Salts. Ernst Beutel (*Chem. Zentr.*, 1916, ii, 638; from *Osterr. Chem. Zeit.*, **19**, 123—124).—Well-defined crystals of chrome alum and cobalt magnesium sulphate were observed to lose water of crystallisation at those places where their surfaces were in contact with a metal support. These spots increase very rapidly in size when the crystals are exposed to light. The loss of weight in crystals exposed to ultra-violet and sun-light was respectively twice and two and a-half times that observed in crystals kept in the dark. H. W.

The Release of Radium Emanation from Water at Different Temperatures by the Bubbling Method. J. Moran (*Trans. Roy. Soc. Canada*, 1916, [III], **10**, 57—66).—Experiments, in which a constant current of air was bubbled through a solution of radium at temperatures ranging from 16·5° to 80°, show that the emanation removed by the air increases with the temperature. When this method is employed in the estimation of the radium content, the solution should be kept at a constant and measured temperature. H. M. D.

Experimental Determination of the Ionisation Potential of Helium. Charles B. Bazzoni (*Phil. Mag.*, 1916, [vi], **32**, 566—575).—According to Bohr's theory, the energy required to remove one electron from a helium atom corresponds with 29·3 volts, whilst previous measurements of the ionisation potential have given 20 to 20·5 volts. In view of the agreement of Bohr's theory with experiment in so many directions, the ionisation potential of helium has been redetermined under conditions which avoid certain errors, which, it was thought, might be the cause of the discrepancy between theory and the earlier observations. The results obtained show that the true ionisation potential is not greater than 20 volts, and to reconcile the value with Bohr's theory it appears to be necessary to introduce new assumptions relative to the mechanism of the ionisation process. H. M. D.

Specific Smell Intensity and the Electrical Phenomenon of Cloud-like Condensed Water Vapours in Chemical Series. H. Zwaardemaker (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 334—340).—Previous experiments have shown that the cloud of condensed water vapour, which is obtained by spraying aqueous solutions, has a positive charge when the dissolved substance is odorous. By comparing the quantities of the aliphatic alcohols and the fatty acids, which are required to arouse olfactory sensation, with the electrical effects produced when aqueous solutions of members of these two series of homologous substances are sprayed, it is found that the smell intensities correspond more or less with the power of the substances to give a positive charge to the water-droplets. It is supposed that both properties are connected with the lowering of the surface tension of water by the substances concerned. H. M. D.

Overvoltage Tables. IV. The Theories of Overvoltage and Passivity. EDGAR NEWBERY (T., 1916, **109**, 1359—1368).—Reviewing the results so far obtained by the author in his investigations of overvoltage (T., 1914, **105**, 2434; 1916, **109**, 1051, 1066, 1107), the conclusion is drawn that overvoltage is probably due to the high solution potentials of compounds of the electrode material with the discharged ion or with a product of the discharged ion. These compounds tend to form solid solutions in the electrode substance, and are usually stable only under the influence of high pressure or high temperatures. Passivity is due to the insolubility and good electrical conductivity of these compounds, which form a protective coating either over the whole metal surface or over the more easily soluble amorphous phase. This coating may consist of the pure compound or of a solid solution of the compound in the electrode substance.

The chemical stability of the higher oxides and hydrides is not to be measured by the overvoltage potentials; it is of more importance than the overvoltage when electrodes are used for the treatment of substances which are only oxidised or reduced slowly. Thus it is possible for an electrode that produces a comparatively stable hydride to effect reductions which another electrode of higher overvoltage is unable to do. For example, oleic acid is reduced at a copper, but not at a lead, electrode; also, nitrates are reduced to ammonia at a copper cathode, but to hydroxylamine at a lead cathode. T. S. P.

Occlusion of Hydrogen by a Palladium Cathode. DONALD P. SMITH and FREDERICK H. MARTIN (*J. Amer. Chem. Soc.*, 1916, **38**, 2577—2594).—The electrical resistance and cathode potential in $2N$-sulphuric acid has been determined for palladium charged with hydrogen up to saturation. The measurements were made in the usual way, both while the wire was being charged electrolytically with hydrogen and after the charging current had been interrupted. It is shown that the proportional increase of resistance at apparent saturation varies widely even with wires made from the same sample of pure palladium. The resistance of saturated wires of 0·1 mm. diameter and less is shown to vary in a well-defined manner with the polarising current, and the resistance after the interruption of electrolysis is shown to undergo reversible and reproducible changes. In the case of wires of 0·32 mm. diameter, none of the above-mentioned changes are observed. It is shown to be probable that the changes of resistance of smaller wires are due to processes occurring within the metal and not far removed from its surface. It is tentatively suggested that hydrogen occluded at the cathode surface exists for some time in a transitional state, in which it possesses an electrical conductance of its own, and passes gradually into another form which has either a much smaller conductivity or none at all. A number of characteristic changes have been observed after the interruption of electrolysis in the cathode potential of saturated palladium wire, and certain connexions have been noticed between the nature and magnitude of these changes and the conditions of electrolysis. A few experiments have been carried out with copper wires which show that this metal does not change its resistance to a measurable extent when subjected to the same treatment as the palladium wires. A single experiment with nickel wire shows that it behaves in the same way as copper in this respect. J. F. S.

Free Energy and Heat Capacity. James M. Bell (*J. Amer. Chem. Soc.*, 1916, **38**, 2629—2630. Compare *J. Physical Chem.*, 1905, **9**, 381).—Polemical. A criticism of Richards's use of some of Marignac's data on heat capacity (Marignac, *Ann. Chim. Phys.*, 1876, [v], **8**, 415). A note answering the criticism and justifying his position is appended by Theodore W. Richards to the paper (*ibid.*, 2631—2632). J. F. S.

The Stem Correction of Thermometers. Edward G. Wheeler (*J. Soc. Chem. Ind.*, 1916, **35**, 1198—1200).—During the course of a continuous distillation, it is frequently impossible, owing to lack of time, to make the necessary calculations for the correction of thermometric readings. To overcome this difficulty, the author has constructed a graph, which is fully reproduced in the original, from which the corrected temperature may be deduced after observations of the actual temperature recorded by the thermometer, the length of the external column, and the temperature of the latter, as determined by an attached thermometer. H. W.

Formula for the Calculation of the Specific Heat of Aqueous-alcoholic Solutions of Different Substances. N. A. Kolosovski (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 84).—The specific heats of aqueous-alcoholic solutions may be calculated by means of the empirical formula $C=1+n(C_0-1)+0{\cdot}004x-0{\cdot}00012x^2+0{\cdot}00000069x^3$, where C is the required specific heat of the aqueous-alcoholic solution of substance A, n the number of gram-equivalents of this substance per 200 mols. of water in the given aqueous-alcoholic solution, x the number of molecules of alcohol per 200 mols. of water, and C_0 the specific heat of an aqueous solution of 1 gram-equivalent of substance A in 200 gram-mols. of water. The value of C_0 is obtained from tables of physical constants. In thirty-four cases in which direct measurements were made of the specific heats of aqueous-alcoholic solutions, the difference between the experimental and calculated values was less than 0·005 in twenty-seven cases and between 0·006 and 0·010 in the remaining seven instances. T. H. P.

Free Energy of Dilution and the Freezing-point Lowerings in Solution of some Salts of Various Types of Ionisation, and of Salt Mixtures. Ralph E. Hall and William D. Harkins (*J. Amer. Chem. Soc.*, 1916, **38**, 2658—2676).—The lowering of the freezing point of aqueous solutions of mannitol, erythritol, sodium iodate, potassium iodate, potassium chloride, potassium nitrate, magnesium sulphate, potassium sulphate, barium chloride, cobalt chloride, and lanthanum nitrate have been determined over a wide range of concentrations. Further measurements have been made of the freezing-point lowerings of equimolecular solutions of mixtures of sodium and potassium iodates, and potassium chloride and nitrate respectively. The temperature measurements were made by means of a fifty-pair thermocouple of copper constantan, and were accurate to 0·0001°. The values $\Delta t/N$ are plotted against the cube root of the concentration, and the degree of ionisation calculated in each case. In the case of mixtures, measurements were made over the range $0·1N$—$0·01N$ for each salt. The values of the degree of ionisation calculated from the results agree well with the mean of similar values of the individual salts. J. F. S.

Freezing-point Lowerings in Aqueous Solutions of Salts and Mixtures of Salts, and of a Salt with a Non-electrolyte. WILLIAM D. HARKINS and W. A. ROBERTS (*J. Amer. Chem. Soc.*, 1916, **38**, 2676—2679. Compare preceding abstract).—Using the method previously adopted, the freezing points of solutions of sodium sulphate, potassium sulphate, and their equimolecular mixture, sodium chloride, and a mixture of mannitol and potassium chloride, have been determined over a range of concentrations. The greatest temperature deviation from the calculated value was found in the case of the mixture of potassium chloride and mannitol, and this amounted to only 6/100000°. J. F. S.

An Improved Ebullioscope. A. SMITS (*Chem. Weekblad*, 1916, **13**, 1296).—A description of an improved form of the author's ebullioscope (*Chem. Weekblad*, 1904, **1**, 469), in which the tendency of the vapour generator to fracture is obviated. A. J. W.

Heat of Combustion of Wood Charcoal. N. I. NIKITIN (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 54—75).—Various methods of drying charcoal to constant weight have been investigated. Satisfactory results are obtained by drying in a desiccator over sulphuric acid, and with charcoal which has been made for some time (a year or more), the dry weight obtained in this way is almost exactly the same as that given by five hours' heating in an oven at 103°, whilst a further heating for three hours is without appreciable influence. On the other hand, charcoal which has been recently prepared exhibits progressive increase in weight when heated at 103°, probably owing to oxidation, which also occurs, although slowly, at the ordinary temperature.

Eighteen samples of charcoal prepared from different kinds of wood, some in heaps and others in furnaces, have been analysed and investigated as to calorific value. The percentage of carbon varies from 73·04 to 92·11, and is always higher in heap charcoal than in retort charcoal; the proportion of hydrogen varies from 0·64% to 4·74%. The heats of combustion, calculated from the compositions by means of either Dulong's or Mendeléev's formula, are always less than the experimental values, and in general the divergence increases with the proportion of oxygen and nitrogen taken together, although the introduction into these expressions of a correcting term is not possible.

Calculation from the author's experimental results shows that the number of calories generated by the combustion of 1 gram of charcoal is given by the expression $80{\cdot}51C+273{\cdot}4H$, C and H representing the percentages of carbon and hydrogen in the dry charcoal. The errors of the values calculated by means of this formula lie between the limits $+0{\cdot}63\%$ and $-0{\cdot}47\%$, and for a sample of brown charcoal containing only 73·04% of carbon, and consisting of partly converted lignin, the error is only $+1{\cdot}48\%$.

T. H. P.

[Heat of Solution in Mixed Solvents.] N. A. KOLOSOVSKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 85—87).—The deductions drawn by Tanatar (A., 1915, ii, 742) from some of the results obtained by the author (A., 1913, ii, 22, 308, 671, 672) are erroneous.

T. H. P.

The Fundamental Values of the Quantities b and $\sqrt{a}$ for Different Elements in Connexion with the Periodic System. III. Discussion of the Different Groups of Elements Separately. J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 287—295. Compare A., 1916, ii, 386, 610).—If the total volume occupied by a liquid at the triple point is represented by v and the real volume of the molecules is b, then $(v-b)/v$ represents the ratio of the free volume to the total volume at the triple point. The evaluation of this ratio is discussed and the formula applied to hydrogen and the inert elements, for which $(v-b)/v$ is thus found to be approximately equal to 1/8.

H. M. D.

The Fundamental Values of the Quantities b and $\sqrt{a}$ for Different Elements in Connexion with the Periodic System. IV. The Elements of the Halogen, Oxygen, and Nitrogen Groups. J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 295—320. Compare preceding abstract).—The values of b_k and $\sqrt{a_k}$ have been calculated for the elements of the fifth, sixth, and seventh groups.

In a discussion of the values of the attraction constant, it is pointed out that the molecular condition of the element in the critical state has a very considerable influence on the value of $\sqrt{a_k}$. In a previous paper (A., 1916, ii, 610) it was suggested that the fact that the observed critical temperatures of certain elements are much higher than those calculated from $T_k=78{\cdot}03a/b$ is due to the high degree of complexity of the molecules of these elements in the critical condition. Such complex molecules, in accordance with the additivity of $\sqrt{a_k}$, would show an abnormally large attraction constant. This view now appears to have been abandoned in favour of the hypothesis that monatomic molecules with free valencies exhibit abnormally large values of $\sqrt{a_k}$. The very high values of the attraction constant for antimony and bismuth are thus supposed to be due to the monatomic condition of these elements in the critical condition. In regard to the other elements belonging to this group, arsenic consists of the mixture of 80% As_4 and 20% As molecules, phosphorus of molecules containing four atoms, and nitrogen of diatomic molecules.

The shadowing effect of univalent atoms on the central ter- or quadri-valent atoms with which the former are in combination is not always complete. If the hydrogen compounds of the elements of the nitrogen group are considered, it is found that the attraction of the central atom is completely eliminated in the case of nitrogen and phosphorus, but the attraction of the much larger arsenic and antimony atoms shows itself to some extent. In the case of arsenic, the diminished value of $\sqrt{a_k}$ is about one-third, and for antimony about one-half, the normal value.

The ratio of the free to the total volume at the triple point decreases from 1/8 for the elements of the helium to 1/20 for the elements of the nitrogen group. It is supposed that this ratio plays some part in determining the transition from the liquid to the solid state. H. M. D.

Thermodynamic Proof of Avogadro's Law. C. DEL LUNGO (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 322—326).—Avogadro's law is the simplest and most natural hypothesis to explain Dalton's laws, but is usually deduced, independently of chemical laws, on the assumption that in gases having the same temperature the mean molecular energy is the same. From this proposition, first enunciated as a postulate by Clausius, and later shown to be a necessary consequence of Maxwell's law, may be derived also Gay-Lussac's law of the identity of the coefficient of expansion for all perfect gases. The postulate of Clausius, together with Avogadro's law as corollary, are thus confirmed by the experimental laws of Gay-Lussac and Dalton, but since the inverse demonstration cannot be made, it cannot be asserted with absolute safety that the postulate is necessary and true; it remains a sufficient and highly probable hypothesis, its probability being increased by various considerations which were advanced by Clausius, and are based on the fact that, when two gases at the same temperature are mixed, the mixture also has this temperature.

The author gives a proof of Gibbs's theorem on the entropy of gaseous mixtures, namely, the entropy of a mixture of gases is the sum of the entropies of the component gases when each occupies the total volume at the same temperature. Assumption of the invalidity of the Clausius postulate then leads to the inadmissible conclusion that a diminution of entropy may occur in a reversible process. This postulate, on which Avogadro's and Gay-Lussac's laws directly depend, is therefore rigorously and simply demonstrated. T. H. P.

A New Method for the Determination of Vapour Densities. X. PHILIP BLACKMAN (*Chem. News*, 1916, **114**, 307).—The bulb in which vaporisation takes place consists of an inverted flask, the neck of which passes through an aperture in the base of a thermostat. H. M. D.

The Application of Vortex Rings in the Determination of Surface Tensions. VIKTOR KUTTER (*Physikal. Zeitsch.*, 1916, **17**, 573—579). The method described depends on the measurement of the period of vibration of drops of the liquid when falling under the action of gravity, and its novelty consists in the device which is adopted for the determination of the time of vibration. The drops are allowed to fall into a second liquid of somewhat greater density, producing vortex rings which penetrate to a depth which depends on the phase of the vibrating drop at the moment when it penetrates the surface of the indicating liquid. By increasing the difference between the level of the tip of the tube at which the drops are formed and the surface of the indicating liquid, this phase may be altered in a continuous manner, and the actual observations consist in determining the difference in the fall which corresponds with a half-period in the vibrating drop. From this difference in the fall, the period of vibration can be easily calculated.

To make the vortex rings clearly visible, the indicator liquid must be suitably chosen, and the particular method described makes use of a solution of some substance which reacts with the dropping liquid or with substances dissolved in this, with the formation of an insoluble substance, which, however, dissolves in excess of the indicator solution. An acidified solution of antimony chloride may thus be used as an indicator for aqueous solutions of many different substances, the vortex ring being rendered visible as the result of the precipitation of antimony oxychloride.

The formation of a precipitate is not necessary, as a matter of fact, and in the case of drops of a solution of potassium permanganate, the vortex rings can be studied with the aid of a solution containing ferrous sulphate and sulphuric acid. In general, the formation of a precipitate affords the most suitable method for observing the vortex rings, and a large number of pairs of solutions, which can be used in combination, are tabulated in the paper. H. M. D.

The Temperature-coefficient of the Free Molecular Surface Energy of Liquids between −80° and 1650°. XV. The Determination of the Specific Gravity of Molten Salts and of the Temperature-coefficient of their Molecular Surface Energy. F. M. JAEGER and JUL. KAHN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 381—397. Compare A., 1916, ii, 126, 128).—The data obtained in measurements of the molecular surface energy of molten salts at various temperatures are recorded. The temperature-coefficients derived from these are given in the following summary, together with the formulæ from which the density (D_4^t) may be calculated. Lithium fluoride, 0·40—0·58, $D=1\cdot798-0\cdot0004375(t-850)$; lithium chloride, 0·47, $D=1\cdot501-0\cdot000432(t-600)$; lithium sulphate, 0·50, $D=2\cdot008-0\cdot000407(t-850)$; lithium nitrate, 0·45, $D=1\cdot755-0\cdot000546(t-300)$; sodium fluoride, 0·52, $D=1\cdot942-0\cdot000564(t-1000)$; sodium chloride, 0·48, $D=1\cdot549-0\cdot000626(t-800)$; sodium bromide, 0·53,

$D=2\cdot306-0\cdot00072(t-780)-0\cdot0^{6}8(t-780)^2$; sodium iodide, 0·29—0·63, $D=2\cdot698-0\cdot001061(t-700)$; sodium sulphate, 0·30, $D=2\cdot061-0\cdot000483(t-900)$; sodium molybdate, 1·2—0·56, $D=2\cdot795-0\cdot000629(t-700)$; sodium tungstate, 0·64—0·98, $D=3\cdot673-0\cdot0009275(t-930)+0\cdot0^{6}337(t-930)^2$; sodium nitrate, 0·24—0·45, $D=1\cdot914-0\cdot000672(t-300)$; sodium metaphosphate, 0·43—1·1, $D=2\cdot193-0\cdot00044(t-800)$; potassium fluoride, 0·33—0·83, $D=1\cdot878-0\cdot000669(t-900)$; potassium chloride, 0·68, $D=1\cdot539-0\cdot0005947(t-750)$; potassium bromide, 0·76, $D=2\cdot106-0\cdot000799(t-750)$; potassium iodide, 1·58—0·41, $D=2\cdot431-0\cdot001022(t-700)$; potassium sulphate, 0·90, $D=1\cdot872-0\cdot000545(t-1100)$; potassium dichromate, 0·86, $D=2\cdot285-0\cdot000695(t-400)$; potassium molybdate, 0·79, $D=2\cdot342-0\cdot00060(t-964)-0\cdot0^{6}128(t-964)^2$; potassium tungstate, 1·6, $D=3\cdot113-0\cdot00082(t-1000)+0\cdot0^{6}162(t-1000)^2$; potassium nitrate, 0·83, $D=1\cdot898-0\cdot0007681(t-300)$; potassium metaphosphate, 0·91—1·28, $D=2\cdot111-0\cdot00043(t-800)$; rubidium fluoride, 1·0—0·40, $D=2\cdot873-0\cdot000967(t-825)-0\cdot0^{6}247(t-825)^2$; rubidium chloride, 1·02, $D=2\cdot129-0\cdot000823(t-700)$; rubidium bromide, 0·77, $D=2\cdot688-0\cdot001096(t-700)$; rubidium iodide, 0·95, $D=2\cdot798-0\cdot001107(t-700)$; rubidium sulphate, 1·98—0·27, $D=2\cdot562-0\cdot000665(t-1050)$; rubidium nitrate, 0·78, $D=2\cdot492-0\cdot000972(t-300)$; cæsium fluoride, 0·72—0·36, $D=3\cdot611-0\cdot001234(t-700)$; cæsium chloride, 0·80—1·70, $D=2\cdot786-0\cdot00108(t-650)$; cæsium bromide, 0·90—0·57, $D=3\cdot125-0\cdot00134(t-650)$; cæsium iodide, 0·82, $D=3\cdot175-0\cdot001222(t-640)$; cæsium sulphate, 1·91—0·43, $D=3\cdot034-0\cdot000711(t-1040)-0\cdot0^{6}494(t-1040)^2$; cæsium nitrate, 1·18—0·42, $D=2\cdot824-0\cdot001114(t-400)$; thallous nitrate, 0·81, $D=4\cdot917-0\cdot00175((t-200)$; stannous chloride, 1·0, $D=3\cdot298-0\cdot001253(t-300)$. In the determination of the densities, a hydrostatic method was employed.

By comparison with organic liquids, for which the normal value of the temperature-coefficient is about 2·24, the above data show that the temperature-coefficient for molten salts is much smaller. Although no general regularity is evident, it seems that for corresponding haloid salts of the alkali metals, the temperature-coefficient has a tendency to increase with the atomic weight of the metal. The low value of the temperature-coefficient of the molecular surface energy of molten salts has frequently been supposed to indicate a high degree of association, but the authors doubt the validity of this conclusion on the ground that such ionised salts do not conform to the requirements of the theory of corresponding states, and that the degree of ionisation varies considerably with the temperature. H. M. D.

The Temperature-coefficients of the Free Molecular Surface Energy of Liquids between −80° and 1650°. XVI. The Surface Tension of some Halogen Compounds of Sulphur, Phosphorus, Arsenic, Antimony, and Bismuth.

F. M. Jaeger and Jul. Kahn (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 397—404. Compare previous abstract).—The temperature-coefficients of the molecular surface energy and the formulæ expressing the variation of the density with the temperature are given in the following summary: sulphur monochloride, 2·24—1·79, D 1·7094 at 0° and 1·492 at 138°; phosphorus trichloride, 1·61, D 1·582 at 16·4° and 1·527 at 46·2°; phosphorus tribromide, 0·81—2·63; arsenic trichloride, 1·40, $D = 2{\cdot}2050 - 0{\cdot}001856t - 0{\cdot}0^{5}27t^{2}$; arsenic tribromide, 2·05—0·98, $D = 3{\cdot}3972 - 0{\cdot}002822(t-25) + 0{\cdot}0^{5}248(t-25)^{2}$; antimony trichloride, 1·66; bismuth trichloride, 2·14—1·78, $D = 3{\cdot}860 - 0{\cdot}00232(t-250)$; bismuth tribromide, 1·76—2·0, $D = 4{\cdot}598 - 0{\cdot}0026(t-250)$.

Although the temperature-coefficient is generally less than the normal value, it is in all cases much greater than the average value obtained for molten inorganic salts. The difference is to be ascribed to the smaller contrast in the electrochemical character of the components and the absence of ionisation.

When the surface tensions of the chlorides or the bromides at the same temperature are compared, it is found that the surface tension increases with the atomic weight of the positive element. This is the reverse of what was previously found in comparing the haloids of the alkali metals.

For the same positive element, the surface tension increases with the atomic weight of the halogen, which is again the reverse of the behaviour shown by the alkali metal haloids. H. M. D.

The Temperature-coefficients of the Free Molecular Surface Energy of Liquids between −80° and 1650°. XVII. The Relations between the Molecular Cohesion of Liquids at their Melting- and Boiling-points and their Absolute Melting- and Boiling-temperatures Respectively. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 405—414).—According to Walden (compare A., 1909, ii, 122), the value of Ma^{2}/T for non-associated substances is equal to 1·156 at the boiling point and 3·65 at the melting point. The material accumulated by the author has been applied in the further investigation of these empirical formulæ. The substances concerned are divided into four groups, the first of which contains 121 compounds, and includes all the substances for which the relation holds approximately so far as the boiling point is concerned. The mean value of $K_{b} = Ma^{2}_{b}/T_{b}$ is 1·12 and of $K_{m} = Ma^{2}_{m}/T_{m}$ is 3·38. The mean value of the constant at the melting point is thus three times that at the boiling point.

The second group contains sixteen organic compounds, for which K_{b} has an appreciably smaller value, and the third group fourteen compounds, for which K_{b} is either much greater than 1·12, or, as in the case of certain glycerides, for which K_{m} is very large in comparison with the normal value. The fourth group includes forty-eight inorganic compounds and metallic salts, and the abnormally small values of K_{m} for the latter show that the empirical relation does not apply at all to molten salts. The halogen compounds of the elements of the nitrogen group approximate much more closely to the requirements of the empirical formulæ. H. M. D.

New Classification of the Processes of Adsorption and Importance of the Theory of Adsorption for Various Branches of Natural Science; Adsorption of Solutions by Porous Substances. M. A. Rakuzin (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 90—94).—From the cases of adsorption which have been previously studied, principally by the author and his collaborators, the following classification of different types of adsorption is deduced.

I. Reversible adsorption: (*A*) Partial adsorption: (*a*) adsorption without separation, most of the adsorptions as yet known being of this type; (*b*) separative or fractionating adsorption, as yet unknown. (*B*) Exhaustive adsorption: (*a*) adsorption without separation, possible examples of this existing; (*b*) separative or fractionating adsorption, the adsorption of the solid paraffins of petroleum by floridin (A., 1915, i, 489) being of this type.

II. Irreversible adsorption: (*A*) Partial adsorption: (*a*) adsorption without separation, examples of which are (1) dyeing with fast dyes, and (2) adsorption of casein from solutions in borax solution by means of aluminium hydroxide; (*b*) separative or fractionating adsorption, as yet unknown. (*B*) Exhaustive adsorption: (*a*) adsorption without separation, examples of this being (1) adsorption of pepsin from aqueous solution by means of aluminium hydroxide, (2) adsorption of α-gelatin, and (3) of β-gelatin by the same adsorbent; (*b*) separative or fractionating adsorption, examples of which are (1) adsorption of egg-albumin from aqueous solution by aluminium hydroxide, (2) adsorption of the peptone of egg-albumin from aqueous solution by the same adsorbent, (3) probably the adsorption of toxins from different serums, the anti-toxins remaining in solution (compare Zunz, *Zeitsch. Immunitätsf.*, 1913, **19**, 326), and (4) adsorption of iodide of starch by aluminium hydroxide.

In a discussion on the practical aspects of adsorptive processes, attention is directed (1) to the removal of the solid paraffins from petroleum, which is thus more easily transported through pipes during the winter, and (2) to the successful application of *Bolus alba* to the treatment of cholera on the Serbian front during the Balkan War of 1913. T. H. P.

Behaviour of Ferric Oxide and Hydroxide towards Aqueous Solutions of Hen's Egg-albumin. M. A. Rakuzin (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 95).—Whereas dry aluminium hydroxide is an excellent adsorbent, and the adsorptive capacity of dry alumina is only three to four times less than that of the hydroxide, neither ferric hydroxide nor oxide exerts any adsorptive action when immersed for twenty-four hours in an aqueous solution of hen's egg-albumin. Since the albumins are adsorbed more readily than other substances, it may be concluded that the latter will not be adsorbed by ferric hydroxide or oxide. T. H. P.

Aluminium Oxide and Hydroxide as Adsorbents and their Behaviour towards Aqueous Solutions of Hen's Egg-albumin. M. A. RAKUZIN and (MLLE.) EK. MAKS. BRAUDO (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 95—97. Compare A., 1915, i, 1015; 1916, i, 90).—Only when chemically pure does aluminium hydroxide exert its full adsorptive power on aqueous solutions of the albumin of hen's eggs. Commercial precipitated alumina is applicable as an adsorbent only when dried to constant weight in a steam oven, such aluminium hydroxide then giving identical results in the hands of different investigators. The adsorptive power is diminished by the presence of moisture. Aluminium oxide exerts only a feeble adsorptive action on albumin solutions. The above conclusions appear to hold also for solutions of other substances than albumin. T. H. P.

Limiting Concentrations in the Adsorption of Aqueous Solutions of Hen's Egg-albumin by Aluminium Hydroxide; Stoicheiometry of Processes of Adsorption. M. A. RAKUZIN, G. D. FLIER, and M. A. BLOCH (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 99—105. Compare A., 1915, i, 1015).—The authors have studied the adsorption at the ordinary temperature of hen's egg-albumin from aqueous solutions of different concentrations by means of aluminium hydroxide, the amount of the latter used being in each case 10% of the weight of the solution. The results obtained show that, when the concentration of the albumin in the solution is equal to or greater than 9%, no adsorption by aluminium hydroxide takes place. The curve connecting the proportion of total albumin adsorbed with the initial concentration of the solution is approximately logarithmic, marked divergence occurring only as the curve approaches the concentration axis. The marked diminution of the adsorption in the latter region is probably related to the increased internal friction of the solution, which renders difficult the penetration of the molecules of the adsorbed substance into the ultramicroscopic capillaries of the adsorbing particles.

Quantitative and exhaustive adsorption occurs only when the quantity of adsorbent is sufficient and its quality suitable; further increase in the quantity is then useless. Between the quantities of adsorbent and adsorbed substance (albumin, paraffin, etc.), the existence of a stoicheiometrical relation is therefore assumed. Such relation is regarded as based on the concentration equation of Ostwald and Freundlich, the quantity of substance adsorbed being inversely proportional to the initial concentration. The results are considered in relation to Freundlich's formula, $x/m=\beta c_1^{1/p}$, where m is the quantity of adsorbent, c_1 the equilibrium concentration, and β and $1/p$ constants depending on the temperature and on the nature of the substance; the values of these constants in the present case are found to be 0·075 and 0·178 respectively. For concentrations of the albumin up to about 6%, the calculated and experimental values of x/m are in satisfactory

agreement, but for higher concentrations the deviations are very considerable.
T. H. P.

The Dissociation Equilibrium of Nitrosyl Chloride, $2NO + Cl_2 \rightleftharpoons 2NOCl$. II. Replacement of the Chemical Constants by Integration Constants calculated from the Molecular Dimensions. MAX TRAUTZ and CLAUS FRIEDRICH HINCK (*Zeitsch. anorg. Chem.*, 1916, **97**, 127—138. Compare A., 1916, ii, 304, and following abstract).—The formerly accepted figures for the heat change in this dissociation are criticised, and it is shown that the value should be about 18,000 cal. instead of 28,800, the integration constant becoming zero instead of 4·9. Values almost identical with these are obtained from the authors' measurements. The equation for the equilibrium then becomes $\log K = -3680/T + 1{\cdot}5 \log T$. The diameter of the intermediate molecule, probably $NOCl_2$, is calculated to be $11{\cdot}6 \times 10^{-8}$ cm.
C. H. D.

The Dissociation Equilibrium of Nitrosyl Chloride, $2NO + Cl_2 \rightleftharpoons 2NOCl$. MAZ TRAUTZ and LILI WACHENHEIM (*Zeitsch. anorg. Chem.*, 1916, **97**, 241—284. Compare preceding abstract). —The former determinations of Trautz and Hinck gave good agreement with theory for the range of temperature 560—590° abs., but not below that range. Using the same apparatus as before, the velocity of dissociation at $T = 273$ and 434 has been determined. The equilibrium has also been determined at temperatures below $T = 500$, using the same apparatus. The measurements show that complete union to form NOCl takes place, but that there is a small further contraction, possibly due to formation of $(NO)_2Cl$. A new apparatus has been designed to admit successive small quantities of chlorine to nitric oxide, and similar experiments have been made in that manner. The heat of formation at $T = 290$ has also been determined calorimetrically, the value $Q_0 = 16{,}841$ cal. being obtained. The conclusions of the investigation are stated in the preceding paper.
C. H. D.

The Dissociation of Phosphorus, and the Detonating Gas Cell in the Light of the New Theory of Gas Reactions and a New Interpretation of the Approximate Additivity of $C_v - \frac{3}{2}R$ for Gases. MAX TRAUTZ (*Zeitsch. anorg. Chem.*, 1916, **97**, 113—126. Compare *ibid.*, 1916, **96**, 1; Stock, Gibson, and Stamm, A., 1913, ii, 43).—The diameter of the P_4 molecule has been recalculated, using Stock's data, and the more probable value of 20×10^{-8} cm. has been obtained.

The usual data for the dissociation of steam lead to improbable values. Reasons are given for doubting the generally accepted values for the degree of dissociation and for the *E.M.F.* of the detonating gas cell, higher values of both being probable.

In applying the principle of additivity, the assumption is generally made that each gas consists of only one kind of molecules. If, however, several 'thermal isomerides' are present, the heat of

isomerisation must be taken into account, and a small correcting term must be introduced. This correction is in most cases so small that satisfactory results are obtained without applying it.
C. H. D.

Diffusion in Liquids. Basil W. Clack (*Proc. Physical Soc., London*, 1916, **29**, 49—57).—The results obtained in previous experiments (A., 1909, ii, 125; 1915, ii, 45) on the diffusion of sodium chloride, potassium chloride, and potassium nitrate in aqueous solution have been recalculated by the introduction of a correction suggested by Griffiths.

A new method is also described of calculating the coefficient of diffusion at any specified concentration from the experimental data. It is said that this gives more certain results than those obtained by the methods previously employed. H. M. D.

Influence of Pressure on Solubility. Herbert F. Sill (*J. Amer. Chem. Soc.*, 1916, **38**, 2632—2643).—By means of a pressure apparatus, which allows of samples being removed without lowering the pressure, the author has determined the solubility of sodium chloride and barium hydroxide in water at 25° under various pressures. A full description of the pressure apparatus is given. The following solubility values are given for sodium chloride at 25° per 100 grams of solution, 26·44 at 1 kilo. pressure, 26·58 at 250 kilos., 26·72 at 500 kilos., and 26·82 at 750 kilos. pressure. In the case of barium hydroxide, the values are 8·304 at 1 megobar, 8·779 at 245 megobars, and 9·366 at 490 megobars pressure. The heat of solution at the saturation point is extrapolated to 51·2 cal. for the octahydrate of barium hydroxide. This value is got from the experimentally found heat changes observed in bringing a 54% saturated solution to 64% and a 64% solution to 74% respectively. Both values were obtained by using the Richards adiabatic calorimeter. The specific volume change per gram of dissolved substance was experimentally determined by a dilatometric method, and found to be 0·0508. Finally, the temperature-coefficient of the solubility was calculated to 0·288%. The whole of the data for evaluation of the equation

$$T(p_2 - p_1)(v_2 - v_1)/(t_2 - t_1) = Q$$

is thus obtained for barium hydroxide. It is shown that the left-hand side of the equation has the value $2·16 \times 10^9$, whilst the right-hand side has the value $2·14 \times 10^9$. J. F. S.

Effect of Salts on the Solubility of Other Salts. VIII*a*. The Solubility Relations of a Very Soluble Bi-univalent Salt. William D. Harkins and Harry M. Paine (*J. Amer. Chem. Soc.*, 1916, **38**, 2709—2714. Compare A., 1912, ii, 28).—The solubility of strontium chloride in water and in solutions of strontium nitrate, sodium nitrate, nitric acid, hydrochloric acid, hydrobromic acid, hydriodic acid, potassium iodide, potassium chloride, cupric chloride, and potassium nitrate of various concentrations have been determined at 25°. The densities of all solutions have also been recorded. Strontium chloride dissolves in water to the extent of 557·6 grams in 1000 grams of water, and the solution has a density D_4^{25} 1·4015. Strontium nitrate increases the solubility to 558·5 grams with 0·1372 equivalent, and then decreases it to 551·4 grams with 3·318 equivs. per 1000 grams of water. Sodium nitrate increases the solubility to 584·8 grams with 3·553 equivs., and then decreases it to 542·6 grams with 6·856 equivs. per litre. Nitric acid has very little influence on the solubility, whereas hydrochloric acid strongly depresses the solubility to 42·09 grams with 9·205 equivs. per 1000 grams. The other substances examined all depress the solubility of strontium chloride appreciably, but not to anything like the extent that hydrochloric acid does. The solubility curve for hydrobromic acid lies above that for hydriodic acid, and hydrochloric acid, on account of its common ion effect, gives a curve which lies much below either. Just as hydrochloric acid depresses the solubility more than hydrobromic acid, so potassium chloride is more effective in lowering the solubility than potassium iodide. The curves for sodium nitrate and nitric acid have the same relative positions as potassium iodide and hydriodic acid and potassium chloride and hydrochloric acid. In all these cases, the solubility of strontium chloride is less in the acid than in the corresponding salt solution.

J. F. S.

Effect of Salts on the Solubility of Other Salts. VIII*b*. Solubility Relations of some Extremely Soluble Salts. William D. Harkins and W. Tudor Pearce (*J. Amer. Chem. Soc.*, 1916, **38**, 2714—2717. Compare preceding abstract).—The solubility of strontium bromide in solutions of strontium nitrate, and of potassium ferrocyanide in sodium ferrocyanide solutions, and sodium ferrocyanide in potassium ferrocyanide solutions of various concentrations, have been determined at 25°. Strontium bromide dissolves in water to the extent of 1066·1 grams per 1000 grams of water at 25°, and the solution has a density D_4^{25} =1·7002. The following values have been obtained for the solubility of strontium chloride in grams per 1000 grams of water in solutions of the following molecular concentrations of strontium nitrate, and the solutions have the appended densities:

Solubility $SrBr_2$...	1066·2	1066·95	1067·42	1068·54	1068·9	1069·17	1073·97
Conc. $Sr(NO_3)_2$ ...	0·0000	0·0360	0·07216	0·14568	0·3066	0·61124	1·8610
D_4^{25}	1·7002	—	1·70325	1·72844	1·73766	1·74866	1·77368

Potassium ferrocyanide dissolves in water at 25° to the extent of 247·96 grams per 1000 grams of water, and the solution has a density D_4^{25} =1·09081. The solubility decreases in sodium ferrocyanide solution until the concentration of the latter reaches 0·12306 mol., after which it continuously increases. Sodium ferrocyanide dissolves in water at 25° to the extent of 207·25 grams per 21000 grams of water, and the solution has a density D_4^{25} =1·0595. The solubility continuously increases in potassium ferrocyanide solution with increasing concentration up to 291·40 grams per 1000 grams of water with 1·0578 mols. of potassium ferrocyanide. J. F. S.

Ionisation and Solubility Relations of Salts of Higher Types. IV. Intermediate Ions in Solutions of Uni-bivalent Salts, and of Lanthanum Iodate, a Ter-univalent Salt.

WILLIAM D. HARKINS and W. TUDOR PEARCE (*J. Amer. Chem. Soc.*, 1916, **38**, 2679—2709. Compare A., 1912, ii, 27, 28, and preceding abstracts).—A theoretical discussion is entered into on the influence of salts of various types on the solubility of a salt of multi-ion type, both on the basis that intermediate ions exist and also that they do not exist. To examine the case experimentally, the solubility of lanthanum iodate, alone and in the presence of lanthanum nitrate, potassium iodate, sodium iodate, sodium nitrate, and lanthanum ammonium nitrate of various concentrations has been determined at 25°. The electrical conductivity and the density of the solutions have also been determined at the same temperature. It is shown that at 25° lanthanum iodate dissolves to the extent of 0·6841 gram per litre, and the solution has a density D_4^{25} 0·998251. In the presence of lanthanum nitrate, the solubility falls continuously with increasing concentration of lanthanum nitrate to a minimum, which is 0·5194 gram per litre with 10·0 millimols. of nitrate, after which it rises to 0·7431 with 200·52 millimols, of the nitrate. In the case of potassium iodate, the solubility falls continuously and reaches the value 0·37388 gram per litre with 1·9828 millimols. Sodium iodate depresses the solubility even more, the value 0·0973 gram per litre being obtained with 6·7989 millimols per litre. Sodium nitrate increases the solubility to 3·030 grams per litre with 3200 millimols. Lanthanum ammonium nitrate also effects a large increase in the solubility. A series of electrical conductivity determinations of all the solutions investigated has also been made. Calculations of the constituents of the mixtures of the solutions were made, and curves drawn to show the changes in the solubility products and concentrations of the non-ionised part with changes in the total ion concentration. In these calculations, intermediate ions are assumed to be non-existent. It was found that the apparent concentration of the non-ionised part is affected normally by the addition of non-common ion salts; it is affected abnormally by the presence of salts having a common univalent ion in that it gives an extraordinary depression, and it is affected even more abnormally by the addition of salts having a common tervalent ion, giving a rapid rise in the apparent solubility. These abnormalities disappear if intermediate ions are assumed to be present. J. F. S.

Neutral Salt Action on Acid Solubilities.

WILLIAM ROLAND HENDERSON and HUGH STOTT TAYLOR (*J. Physical Chem.*, 1916, **20**, 663—679).—The solubility of calcium oxalate in 0·5*N*-solutions of hydrochloric, trichloroacetic, and chloroacetic acids in presence of varying quantities of the corresponding potassium salts has been measured at 25°. Similar measurements were made with calcium tartrate and 0·5*N*-solutions of chloroacetic and acetic acids.

The results show that the salt effect varies according to the strength of the acid, and in general increases with the concentration of the salt. The salt produces an increase in the solubility in the case of hydrochloric acid, a slight decrease when trichloroacetic acid is used as solvent, and a very marked decrease in the case of chloroacetic acid. The reduction of the solvent action is still greater when acetic acid is used, but the salt effect in this case appears to reach a maximum at about 0·1*N*-salt concentration.

The addition of potassium nitrate to hydrochloric acid has very nearly the same effect as the addition of potassium chloride, and a very large positive effect is obtained when potassium chloride is added to the acetic acid solution.

The observed salt effects are compared with those which have been found in the investigation of acid catalysis. The comparison shows that there is some correspondence between the two effects, but that this is by no means complete. H. M. D.

The Interpretation of the Röntgenograms and Röntgen Spectra of Crystals. A. Smits and F. E. C. Scheffer (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 432—438).—The authors criticise the crystal models which have been devised for various substances on the basis of *X*-ray spectroscopic observations. It is pointed out that this method of analysis only gives the distances between the centres of the constituent atoms, and affords no information relative to the actual spaces between the atoms. It is very probable that the distances between the molecules are smaller than the molecular diameter, and it follows that the distance between atoms which belong to different molecules will not be much greater than the distance between atoms in the same molecule. In spite of this approximate equality, the authors contend that the crystal models ought to differentiate between those atoms which are chemically combined in the same molecule and those which are constituents of different molecules. The view that chemical attraction is localised in centres, the number of which is determined by the valency of the atom, is not easily reconciled with configurations which make no distinction between atoms of the same and atoms of different molecules.

A model representing the structure of sodium chloride has been devised in which the valency relations characteristic of the chemical compound are taken into account. This differs from the model put forward by Bragg, but it is claimed that it is equally in agreement with the *X*-ray data. For the details of the space-lattice arrangement the original must be consulted. H. M. D.

Crystals as Molecular Compounds. II. Paul Pfeiffer (*Zeitsch. anorg. Chem.*, 1916, **97**, 161—174. Compare A., 1916, ii, 228).—The diamond is, so far, the only crystal the structure of which as revealed by the *X*-rays accords exactly with the valency of the atom. In this case, the valency and co-ordination numbers are the same. Zinc blende has a very similar structure, but each zinc atom is now symmetrically surrounded by four sulphur atoms, and each sulphur atom by four zinc atoms, as represented by the symbol $[ZnS_4]$ or $[SZn_4]$. The radicle, (RS_4), actually occurs in many thio-salts. That both positive and negative radicles may occur in molecular compounds is shown by the existence of such compounds as $[NR_4][AuCl_4]$. Zinc blende may therefore be regarded as a polymolecular double sulphide, built up according to the rules of co-ordination. In sodium chloride, the co-ordination number is six, and the atoms are placed at alternate cube angles. In accordance with this, all molecular compounds in which the central atom has the co-ordination number six exhibit octahedral grouping.

Fluorite closely resembles blende. Each fluorine atom is symmetrically placed in regard to four calcium atoms, and each calcium atom in regard to eight fluorine atoms. The co-ordination number four corresponds with the general properties of fluorine, whilst the number eight for calcium agrees with the formulæ of such compounds as $[Ca(NH_3)_8]Cl_2$.

Copper and silver have a face-centred cubic lattice, so that each atom stands in similar relation to twelve other atoms, indicating the co-ordination number twelve. Intermetallic compounds may be regarded as molecular compounds, and it is noteworthy that the amalgams contain compounds KHg_{12}, $RbHg_{12}$, $SrHg_{12}$, and $BaHg_{12}$, the number 12 being independent of the valency.

The co-ordination centres may be groups of atoms instead of single atoms. The crystalline structure of anhydrite may be derived from that of sodium chloride by replacing the elementary cube by the rhomb, and then substituting calcium atoms for sodium and SO_4 groups for chlorine. The complex radicles are then $[Ca(SO_4)_6]$ and $[(SO_4)Ca_6]$, the group SO_4 taking the place of a single atom. This replacement of a halogen atom by a bivalent negative group is known in the complex cobalt and platinum salts, such as $[Co(NH_3)_5Cl]X_2$ and $[Co(NH_3)_5(SO_4)]X$. The grouping about atomic radicles as co-ordination centres in place of single atoms may be expected to give less symmetrical structures than in the case of central atoms, and this accords with the fact that anhydrite is not regular, but rhombic. The co-ordination valencies of the SO_4 group are therefore not of equal value. In pyrites, the symmetry is like that of sodium chloride, the groups being $[Fe(S_2)_6]$ and $[(S_2)Fe_6]$. Pyrite is thus to be regarded as a persulphide.

The co-ordination number of both the calcium and the CO_3 radicle in calcite is six. C. H. D.

Mixed Crystals, $(Mg,Zn)SO_4,7H_2O$. C. VIOLA (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 285—299. Compare this vol., ii, 80).—A crystallographic study has been made of heptahydrated zinc and magnesium sulphates, and of their mixed crystals. From the manner in which these crystals undergo alteration in a dry atmosphere, and from the appearance of certain vicinal faces in the mixed crystals and not in the crystals of the pure components, the conclusion is drawn that the mixed crystals, $(Mg,Zn)SO_4 + 7H_2O$, are constituted of alternate very thin layers of $MgSO_4 + 7H_2O$ and $ZnSO_4 + 7H_2O$, yielding a homogeneous and continuous complex. Mixed crystals are therefore homogeneous mechanical mixtures, and not physical mixtures like van't Hoff's solid solutions. Such a conclusion is not contradicted by considerations based either on the total and free energy or on the modern views of crystal structure. T. H. P.

Emulsions and Suspensions with Molten Metals. H. W. Gillett (*J. Physical Chem.*, 1916, **20**, 729—733).—Attention is directed to problems of colloidal chemistry in connexion with molten metals and alloys, and to the importance of these in the metal industries. H. M. D.

Gibbs's Phase Rule. Carlo Viola (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 245—251).—The author discusses the various definitions which have been suggested for phases, and points out that the essential character on which complete agreement exists is that of homogeneity, a break in this indicating passage from one phase to another. As regards homogeneity, however, doubt may occur, since the boundary between homogeneity and heterogeneity must be determined experimentally, and, consequently, depends on the methods of observation available.

Since, therefore, homogeneity is an arbitrary and indefinable character, and use cannot be made of the idea of mechanical separability in the definition of phases, the only remaining character is the principle of energy. If, then, a homogeneous complex is dissolvable with consumption of work, and can resume its original condition with evolution of work, it assumes the character of a phase. Thus a solution (solid or liquid) is a phase, since the solute cannot be separated from the solvent without expenditure of work, and cannot again enter into solution without yielding the same amount of work. The same may be said of homogeneous mechanical mixtures when the very fine heterogeneous particles composing them are not separable without a sufficient expenditure of work. In order to separate two very fine particles in intimate contact, the surface and the surface tension, and hence also the energy, are increased. For this reason a conglomerate or a dissolved mechanical mixture, the heterogeneous components of which have the whole of their contour in contact with the solvent, is not a phase. The properties of the triclinic felspars are in accord with those of either a solid solution or a homogeneous mechanical mixture, and these minerals are to be regarded as phases.

The fundamental conditions on which the phase rule is based are examined, and it is shown that this rule is applicable to the equilibrium of homogeneous mechanical mixtures considered as phases in contact with other phases, provided that they are reversible in any transformation occurring within the existence of the system.

The case of mixed crystals of heptahydrated zinc and magnesium sulphates is considered later (this vol., ii, 79). T. H. P.

The Equilibrium Solid-Liquid-Gas in Binary Systems which present Mixed Crystals. III. H. R. Kruyt and W. D. Heldermann (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 439—447. Compare A., 1910, ii, 195, 837).—The conditions regulating the co-existence of solid, liquid, and gas phases in the system iodine–bromine have been determined by tensimetric observations on various mixtures. The pressure–temperature curve shows a maximum at 23° and a sharp minimum at 44°, whilst the existence of a further maximum at about 100° is indicated. In this system, the compound IBr is formed, and this compound is probably miscible in all proportions with both the components. The pressure–temperature curve with two maxima and an intermediate minimum is supposed to be characteristic of systems in which the components form a series of mixed crystals and a compound which is also miscible with the components. H. M. D.

Equilibrium of the Binary Mixture, Phenol-Aniline, near the Distectic Point. V. Voano (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 76—84).—Lidbury (A., 1902, ii, 242) found that the maximum melting point for this system is shown by the mixture containing 49 mols. % of aniline, and not 50 mols. % of aniline, which would correspond with the pure aniline phenolate. The author finds, on repeated determination of the solidifying point of one and the same mixture, that this temperature sometimes remains constant within the limits of experimental accuracy and sometimes undergoes a distinct change. Thus the mixture containing 49·95 mols. % of aniline gave successively the solidifying points 30·580°, 30·578°, 30·580°, and 30·520°. It is found, further, that in the neighbourhood of the distectic point there are two distinct curves for this system, the maxima corresponding (1) with 50 mols. % of aniline, and (2) with 49·1 mols. % of aniline. The causes of this result are regarded as (1) the slow decomposition of the aniline phenolate on fusion, and (2) the tendency of the phenolate, deposited from the solutions with excess of phenol, to form solid solutions. T. H. P.

Rate of Hydrolysis of Potassium Cyanide in Aqueous Solution. Jan Zawidzki and Tadeusz Mieczyński (*Chem. Zentr.*, 1916, ii, 730; from *Kosmos* (Lemberg), 1914, **38**, 1366—1375).—The authors have studied the kinetics of the auto-hydrolysis of potassium cyanide in aqueous solution at 100°, 110°, and 120°, and are led to the following conclusions: (1) in dilute aqueous solution (0·25—2·0 molar), the reaction $KCN + 2H_2O = H\cdot CO_2K + NH_3$ is of the first order; (2) the temperature-coefficient is normal, the values being about 2·26 at 100—110° and about 2·06 at 110—120°; (3) the presence of an excess of the products of the reaction

(NH_3 and HCO_2K), as well as of other salts and bases, has no appreciable effect on the rate of hydrolysis; (4) organic acids have a feeble, accelerating action; (5) alcohols, particularly glycerol, have a much more pronounced, accelerating action, which appears to depend on intermediate and side reactions. H. W.

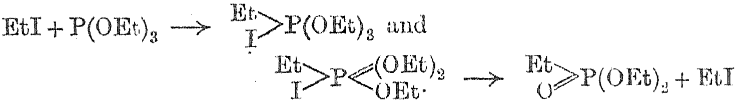
The Kinetics of an Enzymatic Hydrolysis of Glycylglycine. KARL GUSTAV DERNBY (*Compt. rend. Lab. Carlsberg*, 1916, **11**, 263—295).—A quantitative study of the hydrolysis of glycylglycine by ereptase under varying conditions. The enzymatic decomposition of glycylglycine in an alkaline solution causes a diminution in the concentration of the hydrogen ions, the diminution becoming greater as the reaction proceeds. Glycylglycine has a greater dissociation constant (K_a) than glycine itself. The values found were: for glycine, $K_a = 1{\cdot}05 \times 10^{-10}$, $K_b = 1{\cdot}7 \times 10^{-12}$; for glycylglycine, $K_a = 3{\cdot}3 \times 10^{-9}$, $K_b = 0{\cdot}95 \times 10^{-11}$. The ereptase may be regarded as an amphoteric electrolyte, and its activity is notably influenced by variations in the hydrogen ion concentration of the medium. So long as this concentration remains constant and the optimum point is not passed, the scission of glycylglycine by means of ereptase is a unimolecular reaction, provided that the concentration of the enzyme with respect to the substance to be hydrolysed is sufficiently great for autolysis of the enzyme to be neglected. The dipeptide appears to exert a protective action on the enzyme, and thus the autolysis depends on the concentration of the dipeptide. Neither the products of hydrolysis nor the ions $K^{\cdot}$, $Na^{\cdot}$, Cl', Br', F', SO_4', or NO_3' in dilute solutions exert any influence on the velocity of the reaction. The ion ClO_3' tends to check the enzyme action, and the ion $(CN)'$ acts as a strong poison. W. G.

Chemical Dynamics of Autocatalytic Processes. I. Kinetic Theory of Autocatalysis and its Experimental Examination. JAN ZAWIDZKI (*Chem. Zentr.*, 1916, ii, 717—718; from *Anzeiger Akad. Wiss. Krakau*, [A], 1915, 275—318; *Abhand. Akad. Wiss. Krakau*, [A], 1916, **55**, 54—100).—The author discusses the development of the knowledge of autocatalytic phenomena, the discovery of chemical acceleration, the conception of autocatalysis, and of Ostwald's theory of molecular-kinetic autocatalytic action. The more recent experimental investigations on the velocity of autocatalytic reactions in homogeneous and heterogeneous systems and the autocatalytic character of biochemical processes are also described. The results of these investigations confirm, and to some extent extend, Ostwald's theory of autocatalytic acceleration.

A systematic analysis of the available investigations leads the author to the conclusion that the cases of autocatalytic acceleration which have been studied up to the present may be divided into two chief classes: I. Instances of simple autocatalysis in which the velocity of reaction may be expressed by the equations: (1) $dx/dt = k_2x^m(a-x)^n$, and (2) $dx/dt = k_2(a-x)^n/x^m$. II. Instances of compound autocatalysis for which the mathematical expressions are (3) $dx/dt=[k_1 \pm k_2(a-x)^m](a-x)^n$, and (4) $dx/dt=[k_1 \pm k_2 x^m](a-x)^n$, where $(a-x)$ = the concentration of the reacting substance at a definite period, x = the concentration of the reaction product, k_2 = the velocity-coefficient of autocatalytic acceleration, and k_1 = velocity-coefficient of catalytic acceleration.

H. W.

Chemical Dynamics of Autocatalytic Processes. II. Rate of Isomerisation of Triethyl Phosphite. Jan Zawidzki and Wilhelm Staronka (*Chem. Zentr.*, 1916, ii, 718—719; from *Anzeiger Akad. Wiss. Krakau*, [A], 1915, 319—386; *Abhandl. Akad. Wiss. Krakau*, [A], 1916, **55**, 101—167. Compare preceding abstract).—According to Arbusov (A., 1910, i, 802), the isomerisation of triethyl phosphite under the catalytic influence of ethyl iodide occurs in accordance with the equations



$$EtI + P(OEt)_3 \longrightarrow {}^{Et}_{I}{>}P(OEt)_3 \text{ and}$$
$$ {}^{Et}_{I}{>}P{<}^{(OEt)_2}_{OEt\cdot} \longrightarrow {}^{Et}_{O}{\geqslant}P(OEt)_2 + EtI.$$

The authors have investigated the rates of these reactions at 95° and 85° by the dilatometric method, and find that the ethyl phosphinite produces an autocatalytic effect on the process. The reaction therefore presents an example of compound autocatalysis, and the velocity is expressed by the equation $dx/dt=(k_1+k_2 x)(a-x)$.

Further study of the reaction has shown that the ethyl phosphinite only exercises an accelerating effect in the presence of ethyl iodide. The catalytic acceleration due to ethyl iodide and the autocatalytic action of the phosphinic ester are therefore closely connected, and the velocity of the isomerisation processes finds its quantitative expression in the following equation:

$$dx/dt=b/a \,.\, k(1+n'x/a)(1-x),$$

in which a = the original concentration of the ester, b = the concentration of the catalyst, x' = the proportion of isomerised ester, and $n'=a/0{\cdot}2a+0{\cdot}185b$. The values calculated from the second equation are in exact agreement with the experimental results, and the kinetic deductions derived from it can be quantitatively established. The process is therefore the first example of compound, coupled autocatalysis. A normal figure, 2·168, has been found for the temperature-coefficient of the velocity constants, k.

Preliminary experiments in different organic solvents have shown that the kinetic mechanism of the reaction varies with the chemical nature of the medium. In certain indifferent solvents, such as toluene, ethylene dibromide, propyl alcohol, and nitrobenzene, the reaction appears to be of the first order. In chemically active media, such as ethyl or methyl sulphate, on the other hand, reaction also occurs between the ethyl phosphite and the solvent.

Autocatalytic acceleration was not observed in any of the solvents so far investigated, the connexion between catalyst and autocatalyst thus appearing to be broken by the solvent. H. W.

Chemical Dynamics of Autocatalytic Processes. IV. Rate of Hydrolysis of Potassium Methyl Sulphate. JAN ZAWIDZKI and JANUSZ ZAYKOWSKI (*Chem. Zentr.*, 1916, ii, 719—720; from *Anzeiger Akad. Wiss. Krakau*, [A], 1916, 75—158. Compare preceding abstracts).—The authors have investigated the rate of hydrolysis of potassium methyl sulphate in aqueous solution which, at 105—115°, occurs in accordance with the equation $MeKSO_4 + H_2O = MeOH + KHSO_4$. Since the velocity of the reaction is accelerated by the potassium hydrogen sulphate which is formed, the reaction presents a typical instance of simple autocatalysis. The accelerating action of potassium hydrogen sulphate is actually due to the hydrogen ions formed by dissociation of the HSO_4' ions, and since the latter is a very weak acid, the concentration of the hydrogen ions is approximately proportional to the square root of the concentration of the potassium hydrogen sulphate at any given instant. The course of the reaction can therefore be expressed by the differential equation $dx'/dt = k_2\sqrt{a} \,.\, \sqrt{x'}(1-x')$, where a = initial concentration of potassium methyl sulphate and x' = the proportion which has undergone change after an interval of time, t.

The values deduced from the above equation are in complete harmony with the results of experiments on the hydrolysis of pure potassium methyl sulphate at various initial concentrations at 105° and 115°, whilst they also agree satisfactorily with the experimental results obtained in the presence of an excess of the products of the reaction (MeOH or $KHSO_4$) or of neutral potassium salts (KCl and KNO_3). The following regularities are apparent: (1) addition of methyl alcohol exercises a slight retarding effect on the rate of hydrolysis of the ester salt; (2) neutral salts have a feebly accelerating action; (3) normal potassium sulphate has a powerful retarding action, since the dissociation equilibrium, $HSO_4' \rightleftharpoons H^{\cdot} + SO_4'$, is displaced towards the left side. This action of potassium sulphate is approximately proportional to the cube root of its concentration.

Strong mineral acids (HCl and H_2SO_4) have a very marked, accelerating action on the rate of hydrolysis of potassium methyl sulphate, which, in this case, is mathematically expressed by the equation $dx'/dt = k_3/\beta(m + x')(1 - x')$, where $\beta = b/a$, the relationship of the concentration of the added acid to the initial concentration of the ester salt, $m = \beta + \alpha\beta^2/s$, and s is the dissociation constant of the hydrosulphate ion. Weak acids, such as formic and acetic acids, slightly increase the initial rate of hydrolysis, and subsequently have a slight retarding effect. The salts of these weak acids, and also the free bases (KOH), completely alter the kinetic mechanism of the change. In their presence, the hydrolysis of potassium methyl sulphate commenced fairly rapidly; a transitory period of equilibrium then occurred, after which the action became complete in autocatalytic time.

The temperature-coefficient of the velocity constants of the hydrolysis of potassium methyl sulphate in the interval of temperature, 105—115°, is 2·75.

H. W.

A General Twin Series of Varieties of Atoms. A. van den Broek (*Physikal. Zeitsch.*, 1916, **17**, 579—581).—An attempt to show the existence of relations between the different kinds of atoms, which involves the assumption that the ordinary elements are in many cases mixtures of chemically similar, but not identical, varieties of atoms. H. M. D.

Inorganic Chemistry.

Preparation of Hydrogen from Formates and from Carbon Monoxide. G. Gianoli (*Ann. Chim. Applicata*, 1916, **6**, 256—257).—Polemical against Levi and Piva (A., 1916, ii, 525). T. H. P.

The Oxy-Ammonia Flame. D. L. Hammick (*Chem. News*, 1916, **114**, 285. Compare Hodgkinson and Lowndes, A., 1888, 1244).—When an oxy-ammonia flame is obtained in an ordinary blowpipe burner, the characteristic peach-coloured flame is obtained with a small supply of oxygen. On increasing the pressure of oxygen, a livid-white central cone surrounded by a pale peach-coloured luminescent sheath is produced. If the flame is allowed to play on water or ice, nitrates and nitrites can be easily detected in solution. W. G.

The Action of Nitric Oxide on Metallic Peroxides Suspended in Water. Barun Chandra Dutt and Surya Narayan Sen (*J. Proc. Asiatic Soc. Bengal*, 1914, [N.S.], **10**, 287—291).—When nitric oxide is passed into a suspension of lead peroxide in water, a mixture of lead nitrite and nitrate is formed (compare Sabatier and Senderens, A., 1892, 1151, 1271), the nitrate being formed by the oxidation of a portion of the nitrite by the excess of lead peroxide. With barium peroxide in water, nitric oxide yields only barium nitrite. W. G.

The Molecular Weight of Ortho- and Pyro-phosphoric Acid. D. Balareff (*Zeitsch. anorg. Chem.*, 1916, **97**, 139—142. Compare A., 1915, ii, 446; this vol., ii, 23).—Orthophosphoric acid is partly converted into the pyro-acid when kept in a desiccator over phosphoric oxide, or even over sulphuric acid. Orthophosphoric acid has the simple molecular weight in sulphuric acid solution, and if the free acid had the same constitution, it might be expected that the pyro-acid would also be formed on dissolving in sulphuric acid, but this is not the case. Ethyl and methyl orthophosphates have vapour densities corresponding approximately with the simple formulæ. The pyrophosphoric acid molecule is probably simple. C. H. D.

Silicon and its Position in the Thermoelectric Series. II. FRANZ FISCHER and ERNST BAERWIND (*Zeitsch. anorg. Chem.*, 1916, **97**, 56—72. Compare A., 1913, ii, 550).—The difference between the positive and negative varieties of silicon has been attributed to the presence of oxygen in the former. Attempts have now been made to confirm this by analysis. Total silicon is estimated by the fusion method and free silicon by measuring the hydrogen evolved on treatment with potassium hydroxide. It is necessary to grind very finely, and this grinding causes an oxidation of a part of the silicon. The same effect is obtained when a mortar of silicon is used instead of agate. Finely ground silicon oxidises to a notable extent at 210°, so that the oxidation during grinding may be caused by local rise of temperature, aided by the continual formation of fresh surfaces. It has not been found possible to estimate accurately the percentage of oxygen in silicon, even when the substance is dissolved in fused potassium hydroxide in a silver flask, without previous grinding.

The sign of the thermoelectric effect is quite independent of the iron content. The effect is also not due to the presence of aluminium in the positive variety. It is considered that oxygen in solid solution and in very small quantity is responsible for the change of sign. C. H. D.

Oxidation of Carbon by Air at Low Temperatures in Presence of Iron and Other Metals. A. P. LIDOV (*Reprint.* pp. 11. *Charkov*, 1916; from *J. Soc. Chem. Ind.*, 1916, **35**, 1260). —Experiments have been made on the oxidation of finely divided carbon in the air at low temperatures in the presence of lead, nickel, iron, and other metals. Charcoal activated with lead does not lose its activity for a very long time, whereas that activated with nickel or iron loses it rapidly, probably because the metal, precipitated on the surface of the charcoal, becomes converted into its higher oxide. The density of the gas giving a precipitate with barium hydroxide solution, and obtained by the oxidation of carbon activated by means of lead, is always less than that obtained from carbon activated with nickel or iron, and is, on the average, very near to the density of oxan. H. W.

Combination of Carbon and Nitrogen at the Ordinary Temperature. A. P. LIDOV (*Reprint.* pp. 4. *Charkov*, 1916; from *J. Soc. Chem. Ind.*, 1916, **35**, 1260).—In presence of catalytic iron, the first action of air (free from carbon dioxide) on carbon in the cold consists in the gasification of the solid carbon, with formation of the simplest nitrogen–carbon compounds, namely, active α- and inert β-monocyanogen. The oxygen of the air does not take part in the initial stage of the process; this result agrees with those of the author's earlier experiments with pure oxygen in the cold, which showed that, under such conditions, carbon does not undergo the slightest gasification. In the second phase of the process, the α-monocyanogen is oxidised to the stable α-oxan, OCN, and possibly to peroxan, O_2CN, H. W.

Carbon Dioxide from Natural Limestones. A. P. Lidov (*Reprint*, pp. 35. *Charkov*, 1916; from *J. Soc. Chem. Ind.*, 1916, **35**, 1260).—A number of samples of calcspar, aragonite, friable limestones, such as chalk, dense limestones, such as marble, etc., have been decomposed with acid and the density of the evolved gas measured. Variable results were obtained, the values for the gas from calcite being exceptionally low. In explanation of this phenomenon, it is suggested that many limestones contain a more or less considerable proportion of α-oxan, OCN, in addition to the combined carbon dioxide; owing to its ease of formation, α-oxan may be widely distributed. H. W.

Separation of Sodium and Potassium Salts. Spar Chemical Co. (U.S. Pat., 1194465; from *J. Soc. Chem. Ind.*, 1916, **35**, 1261).—To a solution containing, for example, sodium sulphate (90 parts) and potassium sulphate (10 parts), sodium chloride is added in equimolecular proportion to the potassium salt, and the liquid is evaporated until sufficient sodium sulphate has separated to leave an amount of potassium chloride in solution equal to 40% of the total dissolved salts. The mother liquor is then treated with sodium nitrate (in amount equimolecular to the potassium chloride), and the solution is evaporated, whereby sodium chloride and sulphate separate from the hot liquid; these are used for the treatment of a new batch of the mixed sulphates. The potassium nitrate left in the mother liquor is crystallised, leaving sodium chloride and nitrate and about 15% of potassium nitrate in solution; it is separated, redissolved in water, added to the original solution of mixed sulphates (so that equimolecular prôportions of sodium sulphate and potassium nitrate are present), and, on evaporating, potassium sulphate separates, which is removed and washed with hot water. The wash water, containing chiefly sodium nitrate, together with the mother liquor from the potassium nitrate crystallisation, is added to the solution containing 40% of potassium chloride instead of fresh sodium nitrate. The reagents are thus used repeatedly, the only materials separated being sodium sulphate from the first evaporation and potassium sulphate from the last. H. W.

The Double Salts Formed by Sodium and Potassium Carbonates. J. W. Bain and C. E. Oliver (*Trans. Roy. Soc. Canada*, 1916, [iii], **10**, 65—66).—The production of pure potassium carbonate from the ash of seaweeds, wood ashes, and the residues from sugar factories is rendered difficult by the formation of the double salt, $K_2CO_3,Na_2CO_3,12H_2O$. According to dilatometric observations, this double salt decomposes at 35° in accordance with the equation

$$3(K_2CO_3,Na_2CO_3,12H_2O) = 2K_2CO_3 + K_2CO_3,3Na_2CO_3,10H_2O + 26H_2O.$$

The new double salt thus formed appears to decompose at about 130°. H. M. D.

The Dehydration of Sodium Hydrogen Phosphate. D. Balareff (*Zeitsch. anorg. Chem.*, 1916, **97**, 147—148. Compare *ibid.*, 1914, **88**, 135).—Sodium hydrogen phosphate is dehydrated at 250°±2°, even in a very moist atmosphere. This is probably the melting point of the salt. By sealing the salt with water in a glass tube, the volumes being known, the relation between the vapour pressure and temperature may be determined. Fusion is not observed in this case, although pyrophosphate is formed. The salt may be partly dehydrated and converted into pyrophosphate by heating with sulphuryl chloride. C. H. D.

Reduction of Silver Chloride and Lead Chloride. A. Gawalowski (*Chem. Zentr.*, 1916, ii, 723; from *Österr. Chem. Zeit.*, **19**, 150—151).—Precipitated silver chloride is reduced to metallic silver by means of zinc in a few days. $AgNH_3$ gives with zinc and mercury a silvery-grey, dendritic silver tree, whilst with zinc, copper, tin, and mercury it yields at first black, dendritic deposits, which after a time become converted into silver-white dendrites. Scaly, crystalline leaflets of lead are formed by the reduction of aqueous lead chloride by zinc, whilst in the presence of ammonia the lead is precipitated in powdery, black microcrystals. If the deposit containing ammonia is acidified with dilute sulphuric acid, the odour of nitrous acid is observed, and lead is almost instantaneously precipitated in dendritic crystals. H. W.

Silver Peroxynitrate. Mortimer J. Brown (*J. Physical Chem.*, 1916, **20**, 680—700).—When an aqueous solution of silver nitrate is electrolysed between insoluble electrodes, a black substance separates at the anode under certain conditions. This substance has been frequently examined, but its composition is still doubtful. It appears to be decomposed by the nitric acid in the solution as soon as the crystals are detached from the anode.

In the further investigation of the compound, experiments have been made with an electrolytic apparatus which permits of an accurate measurement of the current yield. In this apparatus, the solution is continuously circulated through the decomposition cell, and the decomposing action of the nitric acid is avoided by neutralising the acid by the action of suspended silver carbonate.

From experiments with 5% and 20% silver nitrate solutions and varying current strengths, the silver content of the anode deposit was found to vary between 79·03% and 79·82%, the average being 79·37%. The ratio of the anode deposit to copper deposited in the same circuit varied from 2·69 to 2·98.

These results agree with the formula $2Ag_3O_4,AgNO_3$, which requires 79·9% for the silver content and 2·97 for the coulometer ratio. This is one of the several compounds which have been suggested by the results of previous experiments. The small discrepancies between the calculated and observed silver contents and coulometer ratios are probably due to secondary disturbances.

The current yield numbers show that 10 faradays are required for the deposition of 1 gram-molecular weight of the silver peroxynitrate. H. M. D.

Plaster of Paris. L. A. KEANE (*J. Physical Chem.*, 1916, **20**, 701—723).—The literature relating to plaster of Paris has been examined, and some experiments are described which show that a dead-burned plaster may be transformed into a plaster which sets fairly rapidly with water by grinding so as to obtain particles of very small size. H. M. D.

The Melting Point and Heat of Fusion of Glucinum. G. OESTERHELD (*Zeitsch. anorg. Chem.*, 1916, **97**, 1—6).—Glucinum, prepared electrolytically from sodium glucinum fluoride, is pressed into pastilles and fused in a magnesia tube in hydrogen. The product contains 99·5% Gl, the principal impurity being the carbide. Heating and cooling curves give the value 1278°±5° for the melting point. An approximate determination of the heat of fusion by comparing the duration of the arrests when equal volumes of gold and glucinum are cooled under similar conditions gives 277 cal. per gram, whilst Crompton's rule, atomic weight × heat of fusion ÷ absolute temperature of fusion = 2, gives the value 341. Glucinum has the largest heat of fusion of any metal, corresponding with its high melting point and low atomic weight.

C. H. D.

The Alloys of Glucinum with Aluminium, Copper, Silver, and Iron. G. OESTERHELD (*Zeitsch. anorg. Chem.*, 1916, **97**, 6—40).—Glucinum and aluminium are miscible in the liquid state and do not form a compound. The freezing-point curve has two branches, with a eutectic point at 644° and 4 atomic % Gl. Solid solutions are only formed at the glucinum end of the series up to 3 atomic %. The sections may be etched with dilute sodium hydroxide. For analysis, the quantity available being small and the separation difficult, it is advisable to dissolve in hydrochloric acid and measure the volume of hydrogen evolved, as glucinum gives off about twice as much as aluminium, equal weights being taken, and the composition may then be found by interpolation.

It has not been found possible to alloy glucinum and magnesium, as the latter boils below the melting point of the former. It is not certain whether the metals are miscible or not.

The alloys with copper are complicated. The freezing point of copper is first lowered, solid solutions being formed up to 10 atomic % Gl, and beyond this the liquidus and solidus, which are separated by a very small interval, have an unusual form, passing through a minimum and a point of inflexion. This β-solution breaks up at a lower temperature, there being a eutectoid point at 575° and 31 atomic % Gl. There is a short ascending branch corresponding with the separation of a γ-solution, and then the freezing-point curve rises to a maximum at the composition $CuGl_3$, beyond which it has not been possible to follow the alloys. The δ-solution contains from 70 atomic % Gl upwards. The transformation of β into α and γ is confirmed by quenching experiments. The eutectoid has a structure very like that of the pearlite of steel. The compound $CuGl_3$ is reddish-grey. The alloys may be dissolved in nitric acid for analysis, and the copper estimated by electrolysis.

Silver and glucinum give a simple eutectiferous system, the eutectic point being at 878° and 16 atomic % Gl. Solid solutions are only formed to the extent of about 8 atomic % at the glucinum end of the series. A transformation point at 748° has been observed, and as pure glucinum is not allotropic, it is suggested that a compound may be formed. The alloys increase in hardness and diminish in ductility as the glucinum increases.

The alloys with iron have been examined up to 21% Gl by weight. There is a eutectic point at 1155° and 38·4 atomic % Gl, the region of solid solutions extending to 29%. The β-α-transformation of iron is lowered by glucinum, becoming constant at 650°. The compound, which may have the formula $FeGl_2$, is darkened by sodium hydroxide. C. H. D.

Action of Magnesium on Solutions of Potassium Chloride. Frederick H. Getman (*J. Amer. Chem. Soc.*, 1916, **38**, 2594—2607).—The action of magnesium on water and solutions of potassium chloride has been examined in the following manner. The rate has been determined at which hydrogen is evolved from (*a*) distilled water, (*b*) conductivity water, and (*c*) solutions of potassium chloride of concentrations varying from *N* to 0·1*N*, when strips of magnesium of uniform dimensions are immersed in them. It is shown that the rate of gas evolution is greatly increased by the presence of potassium chloride, but the increase is not proportional to the concentration of the solution. The potential difference between magnesium and solutions of potassium chloride has also been determined. The potential decreases with time in a given solution, and also decreases with decreasing concentration. The hydrogen-ion concentration, both in pure water and in solutions of potassium chloride in which magnesium is immersed, has also been determined. Finally, the concentration of potassium chloride in the solutions after the experiments was determined. The evidence obtained from the experiments has led to the conclusion that the reaction between water and magnesium is to be represented by the equation $Mg + 2H_2O = Mg(OH)_2 + H_2$, and that the presence of the dissolved salt merely accelerates the reaction catalytically. J. F. S.

The Colour of Magnesium Pyrophosphate obtained by Calcining $MgNH_4PO_4,6H_2O$. D. Balareff (*Zeitsch. anorg. Chem.*, 1916, **97**, 149—160).—The grey or black colour often seen in ignited magnesium pyrophosphate is attributed by S. Karaoglanoff (*Jahrb. Univ. Sofia*, 1910—11, **7**) to traces of organic matter accidentally introduced during the precipitation and filtration, but according to this author the coloration is only observed when the pyrophosphate has the dense form which results from incandescence during ignition. Reagents which remove the coloration do so by altering the texture of the precipitate, allowing oxygen to enter and oxidise the carbon.

The colour depends on the water of crystallisation present. The moist, crystallised salt with $6H_2O$ yields a snow-white residue on ignition, but if kept for some weeks over phosphoric oxide, it becomes grey when ignited. There is no appreciable difference of weight between the white and coloured residues, but the grey pyrophosphate is less readily soluble in hot dilute nitric acid than the white variety. The addition of filter-paper fibres to $MgNH_4PO_4,6H_2O$ causes the precipitate to darken on ignition, but if moistened two or three times with water, the residue is white. Dark residues are often obtained even when asbestos is used for filtering. Secondary changes often occur in the precipitation and ignition of the phosphate. The various methods of decolorising the residue give the same results if precautions are taken against loss. Moistening with water and adding a few crystals of ammonium nitrate removes the colour rapidly and completely. C. H. D.

Atomic Weight of Lead of Radioactive Origin. THEODORE W. RICHARDS and CHARLES WADSWORTH, 3rd (*J. Amer. Chem. Soc.*, 1916, **38**, 2613—2622. Compare A., 1914, ii, 653; 1916, ii, 250).—A further set of atomic-weight determinations of lead separated from radioactive minerals. Four sets of results have been obtained from material of different origins, and the following mean results obtained: ordinary lead, 207·18; radioactive lead (Colorado), 207·00; radioactive lead (Australia), 206·34; radioactive lead (obtained from bröggerite, Norway), 206·12; and radioactive lead (obtained from cleveite from Langesund, Norway), 206·08. The most carefully selected sample gave the lowest result, and consequently the authors assume that the higher results obtained from other samples are due to accidental admixture of ordinary lead. As in previous work, no new lines were found either in the ultra-violet or visible spectrum of any of these samples. Hence the atom of lead may be supposed to have a dual structure. Each sample, except the ordinary lead, was radioactive, but the magnitude of the radioactivity seemed to bear no relation to the lowering of the atomic weight. J. F. S.

Some Reactions Involved in Secondary Copper Sulphide Enrichment. E. G. ZIES, E. T. ALLEN, and H. E. MERWIN (*Economic Geology*, 1916, **11**, 407—503).—Copper sulphate solutions react with natural sulphides, a part of the copper being precipitated, this being the process which is concerned in the secondary enrichment of sulphide deposits. The minerals are used either in the form of lumps, so that the colour of the product may be determined, or more often in powder. In the latter case, the powder is sifted through silk bolting cloth, only that part being taken which passes through a cloth with 125 meshes to the linear inch and is retained by a 200 mesh. The finest flour, which adheres to the particles in sifting, is removed by washing with alcohol. The minerals after the experiment are examined microscopically and analysed.

The reactions are carried out at the ordinary temperature in special glass containers in a shaking apparatus, and at higher temperatures in sealed tubes of Jena glass or silica, heated vertically in an oil-bath. When artificial sulphides are to be tested, they are prepared by precipitation and washing, and are dried and heated in hydrogen.

Pyrites is altered to covellite and chalcocite with cupric sulphate solutions. Chalcopyrite and bornite undergo the same change, whilst pyrrhotite is altered to chalcopyrite, and probably to bornite. The order of stability is: chalcopyrite, covellite, chalcocite, the last being the most stable of all, although even it is slowly altered, yielding metallic copper and sulphuric acid. The intermediate products, chalcopyrite and covellite, are most likely to be obtained when a large surface of the original sulphide is exposed to a dilute solution of cupric sulphate. Increased temperature accelerates the reactions without greatly altering their nature, but secondary reactions, such as the formation of cuprous sulphate and hydrolysis to hæmatite, are more marked at higher temperatures. Cuprous sulphate appears to accelerate the reactions. An increased concentration of sulphuric acid retards the above reactions. A reversal of the enrichment reactions has not been observed. Galena is more reactive than any other of the sulphides examined. The enrichment of galena, blende, pyrrhotite, and bornite is accelerated by the presence of sulphuric acid. C. H. D.

Investigations at High Temperatures. X. Aluminium and Carbon. OTTO RUFF and ERNST JELLINEK (*Zeitsch. anorg. Chem.*, 1916, **97**, 312—336).—Aluminium carbide prepared by heating the metal with carbon contains much nitride. Carbon, prepared by crushing the most strongly heated portions of a carbon resistance tube and boiling with hydrochloric acid, contains only 0·08% of ash, and may be heated with aluminium in a carbon crucible in an atmosphere of hydrogen. After half an hour at 2000°, the mass is compact and dark orange in colour. It contains some aluminium, or a carbide rich in aluminium.

For analysis, the carbide is heated with 4*N*-sulphuric acid, and the evolved gases burnt in a copper oxide tube. The insoluble residue in the flask is collected on a Gooch filter, and dried at 300° to remove sulphuric acid. It consists chiefly of carbon and alumina. The filtrate is used for the estimation of aluminium, iron, and silicon in one portion, another portion being taken for the estimation of nitrogen as ammonia. Small quantities of sulphur are estimated in a fresh quantity of carbide by the evolution of hydrogen sulphide. The highest content of aluminium carbide, Al_4C_3, in the product is 83%, with 6·7% of nitride, the remainder including insoluble matter, iron, silicon, and aluminium.

The highest proportion of methane in the gas evolved with hydrochloric acid is 97·5%, the remainder being hydrogen, but as much as 19·2% of hydrogen has been obtained.

Aluminium carbide partly melts, forming aluminium and graphite, a little above 2200°. The proportion of carbon in the vapour increases with the pressure and with the temperature. The analyses are made by the method employed for other carbides, the loss of weight of the solid components being determined (Ruff and Bormann, A., 1915, ii, 461). The impurities are allowed for in the calculation. Aluminium carbide is more stable in the form of vapour than any of the other carbides examined (manganese, cobalt, iron, and nickel). C. H. D.

The Solubility of Aluminium Hydroxide in Solutions of Ammonia and Ammonium Salts. E. H. Archibald and Y. Habasian (*Trans. Roy. Soc. Canada*, 1916, [iii], **10**, 69—70).—The solubility of aluminium hydroxide in ammonia increases at first with the strength of the ammonia solution, reaches a maximum, and then decreases. These relations are supposed to be connected with the formation of a more crystalline modification of aluminium hydroxide in contact with the concentrated ammonia. In presence of ammonium chloride or nitrate, the solubility of the hydroxide is considerably decreased. The addition of potassium nitrate increases the solubility to a marked extent. H. M. D.

Oxidation-reduction Reactions without the Addition of Acid. III. Ferrous Chloride and Potassium Permanganate. A New Method for the Preparation of Colloidal Hydrated Ferric Oxide. Marks Neidle and John N. Crombie (*J. Amer. Chem. Soc.*, 1916, **38**, 2607—2613. Compare A., 1916, ii, 603).—Solutions of ferrous chloride and ferrous sulphate have been titrated with solutions of potassium permanganate without the addition of acid. It is shown that the stoicheiometric relationships are the same as in the oxidation in the presence of acid. In the oxidation of ferrous chloride, it is shown that the collateral oxidation of the chloride ion is practically avoided by adding the permanganate gradually and stirring the solution vigorously. The products of reaction with ferrous chloride are the chlorides of potassium, manganese, and ferric iron, together with colloidal hydrated ferric oxide, whilst with ferrous sulphate the corresponding sulphates are formed, and also hydrated ferric oxide, which is precipitated by the sulphion. One gram-equivalent of potassium permanganate dissolved in about 600 c.c. of water was slowly added to 1 gram-equivalent of ferrous chloride dissolved in a litre of water, and the resulting clear, deep brownish-red solution diluted to 2 litres. This solution remained perfectly clear for several weeks, then gradually became more and more turbid, until finally a suspension separated. Until the latter stage is reached, dialysis yields a perfectly clear, brownish-red sol of hydrated ferric oxide. After the suspension has settled, dialysis gives a hydrated ferric oxide sol which is slightly turbid in reflected light, but perfectly clear in transmitted light. J. F. S.

The Hydrolysis of Iron Ammonium Alum. WILLIAM NORMAN (T., 1916, **109**, 1331—1339).—The precipitate which separates from solutions of ferric ammonium alum on keeping is found to have the composition $2Fe_2O_3,SO_3$. The colours of iron alum solutions alone and in the presence of sulphuric acid, ammonium sulphate, sucrose, potassium chloride, and alcohol have been measured by means of a Duboscq colorimeter, and are shown to be in agreement with the supposition that the colour is due to the presence of a soluble form of the basic sulphate of the composition given above.

The white precipitate obtained on adding concentrated sulphuric acid to a solution of iron ammonium alum is found to be the anhydrous alum. The densities and apparent molecular solution volumes of iron ammonium alum solutions of varying concentrations at 32·5° have been determined. T. S. P.

Cobaltammines. I. Various Ionisation Types as Determined by the Freezing Point Lowering in Aqueous Solution, together with Conductivity Measurements. WILLIAM D. HARKINS, R. E. HALL, and W. A. ROBERTS (*J. Amer. Chem. Soc.*, 1916, **38**, 2643—2658).—The authors have prepared the following cobalt derivatives and have measured the conductivity and lowering of the freezing point of solutions of these salts: hexamminecobalt chloride, nitropentamminecobalt chloride, chloropentamminecobalt chloride, dinitrotetramminecobalt chloride, dinitrotetramminecobalt nitrate, cobalttrinitrotriammine, potassium tetranitrodiamminecobaltate, ammonium tetranitrodiamminecobaltate, and sodium cobaltic nitrite. The freezing point determinations were made in fairly dilute solutions, and the temperature changes measured by means of a fifty-junction differential thermo-element of copper and constantan wire. In each case the freezing point lowerings are compared with those of salts of similar and known ionic type. It is shown that hexamminecobalt chloride, $[Co(NH_3)_6Cl_3]$, is of the same type as lanthanum nitrate–tetraionic; nitropentamminecobalt chloride,

$$[NO_2(NH_3)_5CoCl_2],$$

and chloropentamminecobalt chloride, $[ClCo(NH_3)_5Cl_2]$, are similar to cobalt chloride, tri-ionic in character; dinitrotetramminecobalt chloride and nitrate, $[(NO_2)_2Co(NH_3)_4Cl]$, are similar to sodium iodate–di-ionic salts; trinitrotriamminecobalt is non-ionic. Potassium tetranitrodiamminecobaltate, $[(NO_2)_4Co(NH_3)_2K]$, and ammonium tetranitrodiamminecobaltate, $[(NO_2)_4Co(NH_3)_2NH_4]$, are like potassium iodate, and evidently di-ionic; sodium cobaltic nitrite, $[(NO_2)_6CoNa_3]$, is tetraionic. The degree of ionisation and the ratio $\Delta t/N$ is calculated for each concentration in each case. The electrical conductivity of the above-mentioned compounds, as well as that of magnesium sulphate, have been determined at 0° and 25° for a number of concentrations, and the degree of ionisation calculated. The results show that the type of each salt is that assumed for it by Werner, but the freezing-point measurements do not agree well with those of Werner. There is a large discrepancy, except in the case of trinitrotriamminecobalt, between the present results and those of Petersen (A., 1897, ii, 302; 1902, ii, 126), often amounting to as much as 100%. For these discrepancies the authors are unable to offer any explanation.

J. F. S.

The Occlusion of Iron by the Ammonium Phospho-Molybdate Precipitate. E. H. ARCHIBALD and H. B. KEEGAN (*Trans. Roy. Soc. Canada*, 1916, [iii], **10**, 67—68).—The factors which influence the occlusion of iron by ammonium phosphomolybdate have been examined. In the case of dilute solutions, the amount of occluded iron is independent of the quantity of [illegible]on in the solution, but in more concentrated solutions it increases with the quantity of dissolved iron. For solutions of the same iron concentration, the quantity of occluded iron increases somewhat more rapidly than the concentration of the phosphoric acid. The dilution of the solution has no appreciable influence on the amount of occluded iron when the quantities of iron and phosphoric acid remain the same.

The iron is occluded at the time of precipitation, and is not removed by washing. It is suggested that a definite chemical compound is formed.

H. M. D.

Investigations at High Temperatures. IX. The Preparation of Articles of Zirconia. OTTO RUFF and GEORG LAUSCHKE (*Zeitsch. anorg. Chem.*, 1916, **97**, 73—112. Compare A., 1914, ii, 474).—The fusibility of mixtures of zirconia with other oxides has been determined, using a carbon tube furnace, the atmosphere of the furnace being under a low pressure. Zirconia containing 98·73% ZrO_2, the remainder being silica and iron oxide, melts at 2563°±10°, the temperature of the previous shrinking operation being without influence. Thoria has not been melted in the reducing atmosphere of this furnace, the oxide cracking and giving off fumes at 2450° without fusion. Glucina, alumina, yttria, and thoria are suitable for addition to zirconia, causing little volatilisation, whilst magnesia causes fuming and silica lowers the melting point excessively.

For the preparation of crucibles, the addition of 1% of alumina is recommended for use at 2000°, or 1% of thoria at 2200°, and from 1 to 3% of yttria at 2400°. The addition of larger quantities increases the porosity and has no advantage. Both the porosity and the contraction vary with the temperature of firing. Magnesia and glucina reduce the porosity.

Pure zirconia is readily soluble in hydrofluoric acid at 25°. Zirconium and thorium may be separated in this way, the oxide of the latter remaining insoluble. Details for the preparation and separation of thorium and zirconium fluorides are given.

C. H. D.

Ammoniacal Derivatives of Platinous Nitrite. LEO ALEXANDROVITSCH TSCHUGAEV and STANISLAV STANISLAVOVITSCH KILTINOVIC (T., 1916, **109**, 1286—1295).—Compounds corresponding with the general formula $Pt2NH_3X_2$ or $Pt2AX_2$ (A=amine) are formed by the action of ammonia or of amines on complex salts of the type $[PtX_4]M_2$, but hitherto it has not been ascertained if they have in all cases the same *cis*-configuration. This question, and, more generally, the study of the ammonia compound of platinous nitrite, have now been taken up by the authors.

The addition of ammonia to a cold solution of potassium platinonitrite gives a precipitate of very fine and nearly colourless crystals of the formula $[(NO_2)_2Pt(NH_3)_2]$. Comparison of the physical properties of this substance with those of the known isomeric compounds shows that it consists of *cis*-dinitrodiamminoplatinum. Its constitution was further proved by showing that the compound *cis*-$[Cl_4Pt(NH_3)_2]$ is produced on boiling with concentrated hydrochloric acid, and this can be further reduced to *cis*-$[Cl_2Pt(NH_3)_2]$ by means of oxalic acid. The *cis*- and *trans*-dinitrodiamminoplatinum differ from each other in that the former, on treatment with potassium hydrogen oxalate, readily gives the yellow complex salt, $K_2[Pt(NO_2)_2(C_2O_4)]$, from which the salt,

$$[Pt4NH_3][Pt(NO_2)_2(C_2O_4)],$$

is obtained as orange-yellow needles by precipitation with Reiset's Base I.

Both *cis*- and *trans*-dinitrodiamminoplatinum dissolve in dilute aqueous ammonia on heating, and from the solution potassium platinochloride precipitates nitrotriamminoplatinous platinochloride, $[NO_2Pt(NH_3)_3]_2PtCl_4$, as small, flesh-coloured, glistening plates. The corresponding nitrite, $[NO_2Pt(NH_3)_3]NO_2$, can also be obtained, from which, by appropriate reactions, the *platinobromide*, $[NO_2Pt(NH_3)_3]_2PtBr_4$, deep violet needles, and the *platinonitrite*, $[NO_2Pt(NH_3)_3]_2Pt(NO_2)_4$, pale yellow needles, can be prepared. The nitrite readily loses one molecular proportion of ammonia, giving rise to *trans*-dinitrodiamminoplatinum. T. S. P.

Mineralogical Chemistry.

Lorettoite, a New Mineral. ROGER C. WELLS and ESPER S. LARSEN (*J. Washington Acad. Sci.*, 1916, 6, 669—672).—The new mineral occurs as honey-yellow, slabby masses at Loretto, Tennessee. It has an adamantine lustre and a bladed structure with a perfect cleavage along the blades. D 7·39 is perhaps low, owing to the presence of minute gas cavities, arranged along planes at right angles, which impart a cloudiness to the material. The substance is optically uniaxial and negative ($\omega_{Li}=2·40$, $\epsilon_{Li}=2·37$), and probably tetragonal. Hardness, 3; fusibility, 1. It is readily soluble in hot dilute nitric acid. Analysis by R. C. Wells of nearly pure material gave:

PbO.	Cl.	P_2O_5.	CaO.	MgO.	Al_2O_3.	ZnO.	CO_2.	H_2O.	Insol.	Total, less O for Cl.
93·98	3·98	0·11	0·48	0·56	0·08	0·31	0·20	0·03	0·58	99·41

A second determination of the chlorine gave 4·09%. A specimen in the collection of the University of California, labelled as "massicot," but of unknown locality, has D 7·65 and optical characters identical with those of lorettoite; this contains chlorine, 4·94%. These results approximate to the formula $6PbO,PbCl_2$.

L. J. S.

Cristobalite. Henry Le Chatelier (*Compt. rend.*, 1916, **163**, 948—954).—The author has found crystals of cristobalite in a mass of "quinquet," used for making miner's lamp glasses, in siliceous bricks from the dome of a glass furnace, and in the residues from the manufacture of siliceous bricks which had been heated at 1700°. The formation is explained on the grounds that the quartz dissolves in the fused mass, in some cases at 800°, giving a saturated solution which, maintained at the same temperature for some days, deposits cristobalite, which is less soluble. In the same way, cristobalite may become converted into tridymite, but the process is much slower. The author does not agree with Fenner (compare A., 1913, ii, 133) that from 1480—1780° cristobalite is the stable form and not tridymite, as he failed to get any conversion of tridymite when it was heated at 1700° for some time.

W. G.

The Separation and Thermal Metamorphosis of the Zechstein Salts: Bischofite, Kainite, and Blödite. M. Rózsa (*Zeitsch. anorg. Chem.*, 1916, **97**, 41—55. Compare A., 1916, ii, 257).—The view of Jänecke, that carnallite has been formed by the fusion of a layer of bischofite, which has then penetrated into the lower layers of hard salt and langbeinite, is untenable. Kieserite and carnallite must have been formed by the action of mother liquors rich in magnesium chloride on the solid salts during the drying process. The author's previous conclusions are maintained. C. H. D.

Analytical Chemistry.

The Sulphonephthalein Series of Indicators and the Quinone-Phenolate Theory. H. A. Lubs and S. F. Acree (*J. Amer. Chem. Soc.*, 1916, **38**, 2772—2784. Compare A., 1908, i, 423, 652, 653; 1909, i, 650).—The authors have examined a number of sulphonephthalein compounds prepared by Lubs and

Clark (A., 1916, ii, 44, 570), and examined by White (*Science*, **42**, 101), determining in each case the P_H range and the number of molecules of alkali required per molecule of indicator to raise the P_H value sufficiently to give the intense colour change characteristic of each indicator. The sulphonephthaleins, having no negative groups in the phenol residues, give yellow or orange solutions, their colours and conductivities showing that they exist largely in the quinoidal form. They are "self-indicators" requiring from 0·85—0·98 mol. of alkali before the intense colour change due to the dibasic salt is observed. The monobasic sulphonic acid salt has practically the same colour as the almost completely ionised, free acid. The introduction of negative groups into the benzene-sulphonic acid residue increases the affinity constant of this group, but does not appreciably alter that of the phenol group. All these facts and the experimental data support the quinone-phenolate theory of Acree (*loc. cit.*). The free sulphonephthaleins and their monobasic salts give absorption spectra containing a yellow band characteristic of the quinones. This disappears, and a deep red band appears when the dibasic salt is formed, indicating that the quinone group as such disappears, owing to the formation of a complex quinone-phenolate group.

By substituting bromo-, nitro-, methyl, *iso*propyl, amino-, and other groups in the benzenesulphonic acid group, and in the phenol residue, it is possible to change the ionisation constants of the sulphonic acid and phenol groups, and hence prepare a series of indicators having a wide range of sensibility of hydrogen ions.

W. G.

Control of Water Supplies which have been Chlorinated. Le Roy (*Ann. Falsif.*, 1916, **9**, 339—345).—The iodide-starch reaction is the most sensitive of many reactions which have been proposed for the detection of active chlorine in water. The water to be tested should, however, be cooled to 10° or lower before the reagent is added; at this temperature, 0·00006 gram of chlorine per litre of water will give a reaction, whilst at 20°, 0·0001 gram of chlorine cannot be detected. A reagent which will detect as little as 0·00002 gram of chlorine per litre may be prepared by dissolving 1 gram of hexamethyltri-*p*-aminotriphenylmethane in 10 c.c. of dilute hydrochloric acid (1 : 1), diluting the mixture to 100 c.c., adding animal charcoal, and filtering it; this reagent, which gives a violet coloration with chlorine, is more sensitive at 20° than at 10°, and is less affected by nitrites than is the iodide-starch solution. It does not give a coloration with hydrogen peroxide. A description is given of a colorimeter for use in the estimation of chlorine by means of this reagent. W. P. S.

Reactions for Distinguishing between Perchlorates, Periodates, Percarbonates, Persulphates, and Perborates. A. Monnier (*Ann. Chim. anal.*, 1916, **21**, 237—240).—The solution to be tested should be free from heavy metals, vanadates, tungstates, molybdates, dichromates, and ferricyanides. *Per-*

borates and percarbonates.—The two salts give respectively the usual reactions for boric acid, carbon dioxide, and hydrogen peroxide, and yield a blue coloration when their solution is treated with potassium dichromate and dilute sulphuric acid. If a perborate solution is added in excess to a chrome alum solution, a greenish-yellow precipitate is produced; when the mixture is shaken with the addition of ether and dilute sulphuric acid, the ether is coloured blue. Percarbonates and hydrogen peroxide do not give this reaction. *Iodates and periodates.*—When a solution containing these salts is treated with chloroform and titanium trichloride solution, a white precipitate forms and iodine is liberated, giving a violet solution in the chloroform; chlorates and perchlorates also liberate iodine from an iodide in the presence of titanium trichloride, but a white precipitate is not formed. Periodates can be distinguished from iodates by the silver nitrate reaction, and also by means of an alcoholic benzidine solution, with which the periodate gives a brown coloration. *Chlorates and perchlorates.*—A portion of the solution is treated with potassium bromide, chloroform, and titanium trichloride solution; bromine is liberated in this test by chlorates, but not by perchlorates. The latter, when treated with methylene-blue solution, yield a violet-coloured precipitate which detonates when heated on a platinum foil. To detect chlorates and perchlorates in the presence of iodates and periodates, the last two must be removed by means of silver nitrate, and the excess of silver by potassium bromide, before the tests are applied. Bromates may be detected in the presence of chlorates and iodates by treating the solution with manganous sulphate solution acidified with sulphuric acid; a violet coloration (manganic sulphate) is produced by bromates, but not by chlorates or iodates. *Persulphates.*—In the absence of iodides and perchlorates, persulphates yield a red precipitate with methylene-blue solution. To identify a persulphate in the presence of a perchlorate, an alcoholic benzidine solution is poured on the surface of the solution under examination; a blue precipitate appears at the junction of the two liquids if a persulphate is present.

W. P. S.

Estimation of Fluorine in Soluble Fluorides. J. G. DINWIDDIE (*Amer. J. Sci.*, 1916, [iv], **42**, 464—468).—A neutral solution of the fluoride is heated to boiling and powdered calcium sulphate is added; after one hour, the precipitate, consisting of calcium fluoride and calcium sulphate, is collected on a filter (a disk of filter-paper fitted into a perforated platinum crucible), washed with water saturated previously with calcium fluoride and calcium sulphate, and then washed into an ordinary platinum crucible. The water is evaporated, the disk of filter-paper is ignited, and the ash added to the crucible, and the contents of the latter are then heated at 300° for one hour and weighed. The residue is now sulphated, again heated at 300°, and re-weighed. The difference between the two weights is due to the replacement of 2 atoms of fluorine by the sulphuric acid radicle, and the quantity of fluorine is found by calculation. The error of the method is about 0·1%. W. P. S.

Estimation of Dissolved Oxygen by Winkler's Method. G. Bruhns (*Chem. Zeit.*, 1916, **40**, 985—987, 1011—1013. Compare A., 1916, ii, 49).—The alkali solution used in this method should consist of 1 part by weight of potassium hydroxide, 1 part of sodium hydroxide, and 4 parts of water. A stable thiosulphate solution for the final titration is obtained by adding a quantity of alkali sufficient to make the solution distinctly alkaline towards phenolphthalein. After the manganous sulphate has been added to the water and the precipitate allowed to settle, the greater part of the clear supernatant solution may be drawn off before the potassium iodide and hydrochloric acid are added; owing to the lower dilution thus produced, the results obtained are slightly higher than those found by the usual procedure. When potassium hydrogen carbonate is added to convert the manganous hydroxide into carbonate, the small bubbles of air which appear have no effect on the precipitate. W. P. S.

Estimation of Sulphur in Iron and Steel. H. B. Pulsifer (*J. Ind. Eng. Chem.*, 1916, **8**, 1115—1123).—A bibliography covering 285 original articles relating to the estimation of sulphur in iron, etc., is given, and the methods are classified and briefly discussed. Preference is given to the nitro-hydrochloric acid, the chloric acid, and Bamber's methods. Attention is directed to the influence of sulphur segregation and to the importance of obtaining a representative sample for the analysis. W. P. S.

Folin and Denis's Method for the Estimation of Nitrogen by Direct Nesslerisation, and its Application to Spinal Fluids. R. L. Kahn (*J. Biol. Chem.*, 1916, **28**, 203—209. Compare Folin and Denis, A., 1916, ii, 573).—The author finds that the turbidity sometimes produced in the final liquids for colorimetric comparison by this method may be avoided by filtering before the addition of the Nessler's solution instead of after, as described in the original communication (*loc. cit.*). H. W. B.

Comparison of Methods for Estimating Nitrogen in Soils. W. L. Latshaw (*J. Ind. Eng. Chem.*, 1916, **8**, 1127).—The Gunning method, with the addition of a small quantity of copper wire during the digestion, yielded results which agreed with those found by the Kjeldahl method, and had the advantage that there was no "bumping" during the subsequent distillation of the ammonia. W. P. S.

Estimate of Phosphoric Acid after Citrate Digestion. O. C. Smith (*J. Ind. Eng. Chem.*, 1916, **8**, 1127—1128).—Two grams of the soil are washed on a filter with about 250 c.c. of water, the filter-paper and its contents are then transferred to a flask containing 100 c.c. of neutral ammonium citrate solution, the mixture is heated at 60° for thirty minutes, then filtered, and the insoluble portion washed with water at 60° until free from citrate and soluble phosphates. The filter is now placed in a flask and heated with 10 c.c. of concentrated sulphuric acid and 50 c.c. of dilute nitric acid (1:1) until the nitric acid has been expelled; 2 c.c. of concentrated nitric acid are then added, and the heating continued until sulphuric acid fumes appear, at which point a further quantity of nitric acid is added, and the heating again continued. The treatment is repeated until the solution is colourless, and the phosphoric acid is then estimated in the usual way. A clear solution is usually obtained within one hour by this method of oxidising the filter-papers, etc. W. P. S.

The Acidimetric Estimation of Orthophosphoric Acid. D. Balareff (*Zeitsch. anorg. Chem.*, 1916, **97**, 143—146).—Phosphoric acid usually contains an appreciable quantity of carbon dioxide, from which it is freed in the control experiments by heating for several hours in a gold vessel in a stream of purified air. It is then diluted with water free from carbon dioxide. Wagenaar's method (A., 1911, ii, 931) gives satisfactory results if the lead nitrate is added at the Na_2HPO_4 stage, but not otherwise. In Glaser's method, the third hydrogen ion is titrated by adding calcium, strontium, or barium chloride after the solution has become neutral to phenolphthalein, and again titrating until a permanent red coloration is obtained. This only gives accurate results in the presence of an excess of strontium chloride.

The following method is recommended. The dilute solution is first titrated until the red shade of methyl-orange disappears. The second ion is titrated until phenolphthalein becomes a clear red. The solution is then diluted with water free from carbon dioxide, and a neutral solution of silver nitrate is added. The titration is continued with lacmoid as an indicator. C. H. D.

Estimation of Arsenic in Organic Compounds. Arthur James Ewins (T., 1916, **109**, 1355—1358).—The substance is decomposed by means of concentrated sulphuric acid, as in the Kjeldahl process, and the arsenious acid is estimated iodometrically. Trustworthy results are obtained with all but very volatile compounds, and the working details and a number of examples are quoted in the original. J. C. W.

Estimation of Arsenic in Beer and in Dextrose. C. F. Muttelet (*Ann. Falsif.*, 1916, **9**, 326—330).—The Marsh apparatus is recommended for the estimation of arsenic in beer after the organic substances in the latter have been destroyed by treatment with nitric acid, potassium permanganate, and sulphuric acid. An approximate and rapid estimation of the arsenic may be made by treating a portion of the oxidised beer with Bougault's reagent. For the estimation of arsenic in commercial dextrose, a portion of the sample is dissolved in water and then oxidised, as in the case of beer, the resulting solution being tested in a Marsh apparatus.

Samples of dextrose intended for brewing purposes were examined, and many were found to contain from 100 to 400 mg. of arsenic per kilogram. A maximum limit of 4 mg. per kilogram has been fixed, in France, for the quantity of arsenic allowed in dextrose.
W. P. S.

A Boiling Method for the Estimation of Water-soluble Arsenic in Lead Arsenate. GEORGE P. GRAY and A. W. CHRISTIE (*J. Ind. Eng. Chem.*, 1916, **8**, 1109—1113).—A quantity of 0·5 gram of the lead arsenate is boiled for ten minutes with 200 c.c. of water, the solution filtered, and the insoluble portion washed with hot water. The filtrate is treated with 1 gram of potassium iodide and 4 c.c. of concentrated sulphuric acid, evaporated to about 40 c.c., then diluted to 200 c.c., and any coloration due to the presence of free iodine is discharged by the addition of *N*/20-thiosulphate solution. The mixture is then nearly neutralised by the addition of concentrated sodium hydroxide solution, using methyl-orange as indicator, an excess of sodium hydrogen carbonate is added, and the arsenious acid titrated with *N*/20-iodine solution. The lead arsenate is not hydrolysed or dissolved during the boiling with water, and the method is trustworthy.
W. P. S.

Apparatus for the Extraction of Sulphur from Arsenic Trisulphide Precipitates. KARL NEUMANN R. VON SPALLART (*Chem. Zeit.*, 1916, **40**, 981).—The Gooch crucible containing the precipitate is supported on a triangle placed in a beaker containing a small quantity of carbon disulphide. A funnel, having a short stem which has been fused up, is fitted into the top of the beaker, and is filled with water. When the carbon disulphide in the beaker is heated, the vapour condenses on the outside of the funnel, and the liquid falls into the crucible, where it dissolves any free sulphur contained in the precipitate.
W. P. S.

Estimation of Boron in Boron-Steel. C. ASCHMAN, jun. (*Chem. Zeit.*, 1916, **40**, 960—961).—The boron is separated by distillation with methyl alcohol, the distillate is evaporated in the presence of ammonium phosphate, and the residue is ignited until all excess of phosphoric acid has been expelled and only boron phosphate remains. About 3 grams of the steel are dissolved in dilute sulphuric acid contained in a flask attached to a condenser; a large excess of acid should be avoided. The ferrous sulphate solution is then oxidised by the addition of hydrogen peroxide, and the mixture is distilled nearly to dryness, the distillate being collected in a receiver containing 20 c.c. of water, 0·5 gram of ammonium carbonate, and a few drops of ammonia; this receiver is connected with a second, containing a small quantity of water. Ten c.c. of absolute, acetone-free methyl alcohol are then added to the contents of the distillation flask, and the distillation is continued. The addition of methyl alcohol, followed by distillation, is repeated five times, and a slow current of air is drawn through the apparatus for a few minutes between each distillation. Finally, air is drawn through the apparatus for thirty minutes, the contents of the receivers are then transferred to a weighed platinum basin containing 1 gram of ammonium phosphate, the mixture is evaporated to a syrupy consistence, and then heated at 1000° in an electric furnace until the residue of boron phosphate (BPO_4) is constant in weight. W. P. S.

The Oxidation of Coal. GEORGES CHARPY and MARCEL GODCHOT (*Compt. rend.*, 1916, **163**, 745—747).—When coal is heated at 100° for three hours, it loses in weight an amount equal to the loss in weight on drying the coal in a vacuum at the ordinary temperature, which is the moisture content of the coal. If the heating is continued for three months, there is an increase in weight, due to oxidation, equal to 3—5% of the original weight of the coal, there being at the same time a diminution of 3—13% in the calorific power. The content in ash and volatile substances is not appreciably modified by this prolonged oxidation. It is necessary therefore to make a direct determination of the calorific power of a coal to ascertain its value as a fuel. W. G.

[Estimation of the] Total Carbon in Soil by Wet Combustion. C. J. SCHOLLENBERGER (*J. Ind. Eng. Chem.*, 1916, **8**, 1126).—Slight modifications of a method proposed by Ames and Gaither (A., 1914, ii, 676) are recommended. A mixture of sulphuric and phosphoric acids with chromic acid is used for the oxidation, and the carbon dioxide formed is absorbed in barium hydroxide solution. The barium carbonate is titrated as described by Cain (A., 1914, ii, 577), or the excess of barium hydroxide is titrated according to Truog's method (A., 1916, ii, 113).
W. P. S.

Apparatus for the Estimation of Rare Gases (Argon). AD. SIEVERTS and RICH. BRANDT (*Zeitsch. angew. Chem.*, 1916, **29**, 402—406).—An apparatus for the estimation of argon by means of metallic calcium is described, the method depending on the fact that calcium at 450° to 550° absorbs nitrogen and all other gases with the exception of those belonging to the argon group. The apparatus consists of a tube containing the metallic calcium and attached to a manometer; three-way taps are provided at the top of the two arms of the manometer, and connect with tubes for exhausting the apparatus, for admitting the gas, and for admitting air to one of the arms. About 5 grams of calcium are placed in the tube, the latter is placed horizontally in a small oven, heated at 450° to 550°, and the air is exhausted from the apparatus; the tube is then cooled, turned to a vertical position, and placed in a vessel containing cold water. The gas under examination is now admitted, the pressure noted, the calcium tube is again heated as before, and when the pressure no longer decreases (the absorption requires about one hour), the tube is cooled and the pressure again noted. If P was the original pressure and p the final pressure, the gas under examination contains $100p/P\%$ of rare gases by volume. If the gas contains a large proportion of carbon monoxide, carbon dioxide, methane, etc., it should be subjected to a preliminary purification, but when only air is present in addition to rare gases, the mixture may be treated directly. W. P. S.

Oxidimetric Estimation of Cuprous Oxide Precipitated during the Analysis of Sugar with Fehling's Solution. J. Rolle (*Chem. Zentr.*, 1916, ii, 693—694; from *Zeitsch. Spiritusindustrie*, 1916, **39**, 272).—The process depends on the reaction

$$Cu_2O + Fe_2(SO_4)_3(NH_4)_2SO_4 + H_2SO_4 = 2CuSO_4 + FeSO_4(NH_4)_2SO_4 + FeSO_4 + H_2O.$$

The requisite solutions are obtained (1) by dissolving potassium permanganate (5 grams) in water and making the solution up to 1 litre, the solution being standardised after a few days, and (2) by dissolving ferric ammonium alum (80 grams) in water (800 c.c.), filtration through glass wool, addition of concentrated sulphuric acid (50 c.c.), and of water sufficient to bring the volume of the solution to 1000 c.c. The sugar solution is treated in the usual manner with Fehling's solution, and the clear liquor decanted through an Allihn filter tube; the precipitated cuprous oxide is washed with hot water, allowed to subside, and the liquid again filtered. The cuprous oxide is now dissolved by first slowly drawing 50 c.c. of ferric ammonium alum solution through the filter, and then adding the filtrate to the main bulk of the cuprous oxide and heating to boiling, when the cuprous oxide dissolves completely. Potassium permanganate is then added to the boiling, bluish-green solution until a permanent brownish-green coloration is obtained. H. W.

Oxalate-Iodide Process for Paris Green Analysis. C. A. Peters and L. E. Fielding (*J. Ind. Eng. Chem.*, 1916, **8**, 1114—1115).—A method which yields trustworthy results consists in precipitating the copper as oxalate and titrating the oxalate with permanganate; the filtrate from the copper oxalate precipitate is treated with an excess of sodium hydrogen carbonate, and the arsenic then titrated with iodine solution. The details of the method are as follows: 0·25 gram of the sample is boiled with 50 c.c. of water and 1 c.c. of dilute sulphuric acid (1:10) until dissolved, 2 grams of solid oxalic acid are added to the hot solution, and, after eighteen hours, the copper oxalate is collected on an asbestos filter and washed. The filter and precipitate are then transferred to a beaker, heated with 10 c.c. of sulphuric acid (1:1), and the solution is titrated with standardised permanganate solution. W. P. S.

Estimation of Chromium in Ferrochrome. Wilh. Herwig (*Chem. Zentr.*, 1916, ii, 693; from *Stahl u. Eisen*, 1916, **36**, 646—650).—The volumetric estimation of chromium in ferrochrome by means of potassium permanganate gives low results if the theoretical titer number for chromium as recorded in the textbooks (0·310 instead of the empirical number 0·3165) is used. On the other hand, accurate results are obtained by the sodium thiosulphate and potassium dichromate methods. The following shortened sodium thiosulphate process gives results accurate to 0·3%, and can be completed in an hour. The specimen is passed through a sieve of 2700 meshes to the sq. cm.; 0·5 gram of the product so prepared is fused in an iron crucible with sodium peroxide (5—6 grams), gentle heating being used for about a minute until the metal has dissolved in the fused mass, after which it is heated, with gentle agitation, for two minutes with the full Bunsen burner. The somewhat cooled crucible is transferred to a beaker containing about 350 c.c. of water at 60—80°, the beaker immediately covered with a clock-glass, and the water cautiously boiled for five minutes to decompose the sodium peroxide completely; after being cooled, the solution is diluted to 500 c.c. and passed through a double filter. One minute after dilution of 100 c.c. of the filtrate to about 300 c.c. with water, and addition of potassium iodide (1 gram) and hydrochloric acid (D 1·124, 40 c.c.), the titration is effected with sodium thiosulphate.

Decomposition of ferrochrome by magnesium carbonate mixture is frequently incomplete. After being sieved, the specimen should be ground for two to three hours in an agate mortar, and the mixture must be heated for at least an hour with a powerful blowpipe flame. The residue from the first operation must be once more, at least, similarly treated. H. W.

The Physical Character of Precipitated Lead Molybdate and its Importance in the Estimation of Molybdenum and Lead. Harry B. Weiser (*J. Physical Chem.*, 1916, **20**, 640—662).—The precipitation of lead molybdate has been examined with a view to its employment in the estimation of lead and molybdenum.

The precipitate obtained by mixing solutions of ammonium heptamolybdate and lead acetate, or the lead salt of any weak acid, is bluish-white in colour, flocculent, and bulky, and in this form it is unsuitable for quantitative work. A precipitate of similar character is obtained when solutions of sodium molybdate and any soluble lead salt are mixed. On the other hand, the precipitate obtained from solutions of ammonium heptamolybdate and the lead salt of any strong acid is more granular and much less bulky, and has a yellowish-white colour. A similar precipitate is thrown down with all lead salts if a little nitric acid or an excess of sodium or ammonium acetate is added to the solution of sodium or ammonium molybdate before precipitating. Since freshly precipitated lead molybdate is freely soluble in nitric and other strong acids and slightly so in sodium and ammonium acetate solutions, the above-described results can be readily explained in terms of this solvent action.

Lead molybdate tends to absorb ammonium molybdate from solution, and this effect is sufficiently pronounced in the case of the flocculent modification to cause a darkening of the precipitated salt when this is gently ignited. This is due to the decomposition of the ammonium molybdate, which forms a blue oxide when heated at about 200°.

In presence of an excess of ammonium molybdate, the lead salt yields a colloidal solution, from which, however, the lead molybdate is precipitated in presence of a little nitric acid. The coagulation of the negative colloid is attributed to the neutralisation of the negative charge by the adsorption of hydrogen ions.

The above results indicate the conditions which are required for quantitative precipitation of lead molybdate, and detailed instructions are given for the application of the method in the estimation of both lead and molybdenum. H. M. D.

Electroanalysis of Tin without Platinum Electrodes. T. Batuecas (*Anal. Fis. Quim.*, 1916, **14**, 495—511).—An application of Guzmán's method with a copper cathode and a graphite anode to the estimation of stannous and stannic tin in salts and of the metal in alloys. Hydrochloric acid is employed as electrolyte in the estimation of the salts, a mixture of this acid with tartaric acid in the separation of tin from zinc and from cadmium, and an ammoniacal tartrate solution in the separation of tin from silver. A. J. W.

Microanalysis of Wine. Maximilian Ripper and Franz Wohack (*Chem. Zentr.*, 1916, ii, 696—697; from *Zeitsch. landw. Versuchs-Wesen. Österr.*, 1916, **19**, 372—381).—Wohack's method of estimating glycerol in wine (A., 1915, ii, 589) is critically discussed, and has been modified to render it suitable for microanalysis. 0·5 C.c. of wine which has been evaporated to half its original volume and treated with barium acetate and tannin (100 c.c. of wine, 10 c.c. of barium acetate solution [10%], and as much tannin as can be placed on the point of a knife) is brought into the decomposition flask and treated with 1·5 c.c. of hydriodic acid (D 1·96). The decomposition vessel is a quartz or glass tube filled with platinised quartz or platinised asbestos, and is shielded from direct contact with the flame by asbestos paper and iron gauze. The rest of the process is the same as that previously described. The complete process, including evaporation of the wine, occupies one and a-half hours, and gives very accurate results with a minimum expenditure of time, labour, and cost. H. W.

Estimation of Sugar in Blood. Charles G. L. Wolf and Walter C. Ball (*J. Roy. Army Med. Corps*, 1916, **27**, 691—703).—Criticism of Bang's micro-method (compare A., 1907, ii, 136; 1908, ii, 235, 739). Various modifications have been tried, and the following, using titanium trichloride, has been adopted (compare Knecht and Hibbert, A., 1903, ii, 509, and "New Reduction Methods in Volumetric Analysis," pp. 46—47).

The blood (0·1—0·2 gram) is absorbed and weighed in a brush of glass wool and aluminium wire, and is washed out twice with 5 c.c. of 22% potassium chloride in $N/125$-hydrochloric acid. The solution is filtered from glass fibres through asbestos or through a quantitative filter-paper, and the filtrate is heated with a few c.c. of a diluted Fehling's solution (10 c.c. of each of the ordinary pair of solutions are mixed and diluted to 100 c.c.). The heating takes place in a 60 c.c. flask provided with a stout rubber tubing over the mouth, first over a naked flame to incipient ebullition (25 secs.), and then on a sand-bath (gentle boiling for two and a-half minutes). The rubber mouthpiece is then clipped with forceps, and the flask is cooled. About 4 c.c. of *N*-hydrochloric acid and an accurately measured volume (1·5—2 c.c.) of titanium trichloride solution are added. (The latter is prepared by boiling 50 c.c. of the commercial 20% solution for one minute with 100 c.c. of concentrated hydrochloric acid, and making up to 2 litres; it is stored as described in Knecht and Hibbert's book.) Subsequently, 4 c.c. of 50% ammonium thiocyanate are added as indicator, and the solution in the flask is titrated with a ferric solution containing 1/400 gram atom per litre (prepared by oxidising 0·9805 gram of ferrous ammonium sulphate by boiling in slightly alkaline solution with a slight excess of hydrogen peroxide for ten minutes, adding 20 c.c. of concentrated hydrochloric acid, and making up to 1 litre). One c.c. of this ferric solution = 0·107 mg. dextrose.

The estimation is thus indirect and based on the determination of the unreduced copper, which is reduced by titanium trichloride, and the excess of the latter is titrated with the ferric solution. Nevertheless, the method is advantageous in having a sharper and more permanent end-point than that of Bang's iodometric one.

G. B.

Gravimetric Estimation of β-Hydroxybutyric Acid. DONALD D. VAN SLYKE (*Proc. Soc. Exp. Med., New York*, 1916, **13**, 134; from *Physiol. Abstr.*, 1916, **1**, 197).—If β-hydroxybutyric acid is oxidised with potassium dichromate in the presence of sulphuric acid and mercuric sulphate, a precipitate of the acetone compound of mercuric sulphate can be obtained in an amount proportional to the acid present. If 175 c.c. of a β-hydroxybutyric acid solution containing 9% of sulphuric acid, 2% of mercuric sulphate, and 0·25 gram of potassium dichromate are boiled under a reflux condenser for one hour, 7·7 mg. of the mercury-acetone compound are precipitated for each mg. of acid present. The acid may vary from 1 to 9 mg. without affecting the ratio if the concentrations of the other reagents are kept constant. G. B.

Modified Benedict and Hitchcock Uric Acid Standard Solution. L. J. CURTMAN and M. FREED (*J. Biol. Chem.*, 1916, **28**, 89—92).—The substitution of boric acid for acetic acid in the preparation of the standard uric acid solution (compare Benedict and Hitchcock, A., 1915, ii, 602) is advisable in cold weather, because the uric acid does not then crystallise out so readily. In warm weather, however, the modified standard deteriorates more rapidly than the original acetic acid standard. H. W. B.

Systematic Detection of Thiocyanates. LOUIS J. CURTMAN and BEN R. HARRIS (*J. Amer. Chem. Soc.*, 1916, **38**, 2622—2629).—The sensitiveness of the reaction between thiocyanate and ferric chloride has been investigated, alone and in the presence of iodide, acetate, and nitrite. It is shown that 0·1 mg. of thiocyanate may be detected by means of ferric chloride. It is also shown that 7 mg. of iodide, 18 mg. of acetate, and 14 mg. of nitrite yield the same colour with ferric chloride as does 0·1 mg. of thiocyanate. These quantities therefore represent the limiting amounts which may be present in mixtures in which thiocyanate is to be detected. For the detection of thiocyanates, the authors recommend the following procedure. The solution is rendered just alkaline with sodium hydroxide, and excess of barium nitrate, calcium nitrate, and cobalt nitrate is added, and 3 grams of washed asbestos fibre. The mixture is boiled for half a minute, with vigorous stirring, filtered on a fluted paper, and washed until the filtrate is only faintly pink. The filtrate is acidified with five drops of 10% nitric acid, and excess of silver nitrate added. The mixture is boiled for a minute, filtered, and washed until the washings are no longer pink. The filter-paper and contents, containing the chloride, iodide, and thiocyanate, is treated with 10 c.c. of 5% sodium chloride solution, and the mixture kept at the boiling point for five minutes and filtered. The filtrate is concentrated to 4 c.c., treated with a drop of nitric acid (10%), and 0·5 c.c. of 2*N*-ferric nitrate solution. The presence of thiocyanate is indicated by the usual blood-red coloration. An approximately quantitative method for estimating thiocyanates is based on the discharge of the blood-red colour by a solution of mercuric chloride. It is shown that the reaction is better if the ferric thiocyanate solution is titrated with mercuric chloride until a definite standard brown tint is produced, and not until complete discharge of the colour has been obtained. A large number of tests are quoted to show the trustworthiness of the test under different conditions. J. F. S.

Halogenation. XIII. Methods of Estimation of Semicarbazide, Semioxamazide, and Oxalylhydrazide by their Interactions with Halogens and Halogen Oxyacids. RASIK LAL DATTA and JOGENDRA KUMAR CHOUDHURY (*J. Amer. Chem. Soc.*, 1916, **38**, 2736—2739. Compare A., 1914, ii, 504).—The authors now note that if a solution of semicarbazide chlorate is allowed to evaporate in a vacuum desiccator, instead of being decomposed on a water-bath, the chlorate is formed, and as soon as it assumes the solid state, it explodes violently. Attempts were made to isolate semicarbazide nitrite by the interaction of semicarbazide hydrochloride and silver nitrite, but the only product was carbamide.

Semioxamazide is decomposed in the same way as semicarbazide by the action of potassium bromate, iodate, or periodate in the presence of dilute sulphuric acid, three-fourths of its total nitrogen being liberated. With bromine water or sodium hypobromite, the whole of the nitrogen is liberated. Oxalylhydrazide is also decomposed by all these reagents, the whole of its nitrogen being liberated in every case. $C_2O_2(NH\cdot NH_2)_2+2O_2=CO+CO_2+3H_2O+2N_2$.

Potassium chlorate and dilute sulphuric acid do not cause any of the above oxidations. W. G.

Estimation of Theobromine and Caffeine in Cacao and Chocolate. G. Savini (*Ann. Chim. Applicata*, 1916, **6**, 247—250).—The following method, tested on artificial mixtures and on natural products, is found to give satisfactory results.

Twelve grams of the powdered cacao or chocolate are boiled with 70 c.c. of light petroleum on a water-bath in a flask of about 500 c.c. capacity for ten minutes, the hot solvent being decanted on to a small filter, and the operation repeated twice with fresh quantities of light petroleum. The solvent is removed by heating the flask containing the defatted substance, and also the funnel, in an oven for a few minutes. The filter-paper is then placed in the flask, together with 5 c.c. of 10% sulphuric acid and about 250 c.c. of water, and the whole boiled under a reflux condenser for an hour. The hot liquid is introduced into a 300 c.c. measuring flask, together with the hot water used for rinsing out the flask, the filter-paper being prevented from entering. The solution is not cooled to lower than about 30°, and is then made up to volume and filtered. Of the filtrate, 250 c.c., corresponding with 10 grams of the original material, are evaporated to a syrup in a porcelain dish with 10 grams of fine sand and sufficient magnesia to render it distinctly alkaline. The syrup is mixed with a further quantity (8—10 grams) of magnesia so as to give a dry, pulverulent substance, which is scraped off with a spatula and powdered. The powder is treated in a flask with 100 c.c. of chloroform, the pestle, spatula, and dish being washed twice with 5 c.c. of hot water, and the latter added to the chloroform, which is boiled with 0·25 c.c. of concentrated ammonia solution for fifteen minutes in a reflux apparatus. The boiling chloroform is filtered through a pleated filter-paper, and the residue in the flask boiled again with four separate quantities of 100 c.c. each of chloroform. The whole of the filtered chloroform is distilled off on a water-bath, the last traces of the solvent being removed by drying the flask in an oven. The residue is washed with two successive quantities of 10 c.c. of light petroleum, which is decanted on to a small filter, and is then dissolved in a little boiling water, which is filtered through the same filter into a tared platinum or glass dish. The flask is rinsed out three times with small quantities of boiling water, and the whole evaporated on a water-bath, the residue being dried for an hour in an oven at 100° and weighed. The weight of the dry residue, multiplied by ten, gives the percentage of alkaloids (theobromine and caffeine) in the original material. The alkaloids thus extracted are almost colourless and of sufficient purity, the proportion of mineral matter in them being inappreciable. T. H. P.

A Biological Method for the Estimation of Choline. Hermann Führer (*Biochem. Zeitsch.*, 1916, **77**, 408—414).—The isolated heart of a frog is a better subject for the biological estimation of choline (in the form of its acetyl derivative) than is the loop of intestine of a guinea-pig, which has hitherto been chiefly used for this purpose. As many as twenty experiments can be carried out in a day by this method. Acetylcholine is about 100,000 times more active as regards the frog's heart than is choline itself. The paper is illustrated by several chymographic records illustrating the action of acetylcholine. S. B. S.

A Hitherto Neglected Factor affecting the Estimation of Minute Quantities of Creatinine. Andrew Hunter and W. R. Campbell (*J. Biol. Chem.*, 1916, **28**, 335—348).—McCrudden and Sargent (A., 1916, ii, 587) have recently directed attention to the untrustworthiness of creatinine estimations by Folin's method, because of the development of a red colour by the interaction of picric acid and sodium hydroxide in the absence of any creatinine. The present authors find that this occurs only when the picric acid solution has been kept for a considerable time, and is due to the production of a chromogenic substance from the picric acid by the action of light, with possibly other agencies. When the picric acid solutions are preserved in the dark, they may safely be employed for creatinine estimations within a period of at least two months; otherwise, picric acid solutions more than a month old should not be employed. When this precaution is attended to, the Folin method is found to possess a high degree of accuracy.

The authors have also prepared curves showing the actual relation of colour intensity to creatinine concentrations which enables the colour comparisons to be made over a wider range than is generally considered permissible. H. W. B.

Detection of Albumin in Urine. Eicke (*Chem. Zentr.*, 1916, ii, 697; from *Deut. med. Woch.*, 1916, **42**, 1039).—Pandy's reaction has been recommended by Liebers (A., 1916, ii, 594) for the detection of albumin in urine. The author finds, however, that the method is not sufficiently sensitive for this purpose. The limit at which a distinct reaction is obtained lies at 0·2%. Lack of sensitiveness is attributed to the fact that phenol only indicates the presence of globulins, and does not react with serum-albumin.

H. W.

A Test for Albumin for Use by the Military Surgeon. Adolf Edelmann (*Chem. Zentr.*, 1916, ii, 524; from *Wien. Klin. Woch.*, 1916, **29**, 901).—Resorcinol is a suitable reagent for the detection of albumin during campaign.

A small quantity of resorcinol is dissolved in the minimum amount of spring water, and the solution is covered with a few c.c. of urine; a white ring at the junction of the layers shows the presence of albumin. If the urine is added drop by drop to the resorcinol solution, the presence of albumin is indicated by an intense turbidity. The test is more sensitive than the potassium

ferrocyanide or sulphosalicylic acid reactions, and is not vitiated by the presence of any normal or pathological constituent of urine.
H. W.

Certain Methods for the Study of Proteolytic Action. H. C. SHERMAN and DORA E. NEUN (*J. Amer. Chem. Soc.*, 1916, **38**, 2199—2216. Compare Long and Barton, A., 1914, ii, 827; Harding and MacLean, A., 1916, ii, 459).—A comparative examination of some eight different methods for the measurement of proteolytic action. The methods tested were: (1) the Mett method (compare Cobb, A., 1905, ii, 466); (2) estimation of total nitrogen in the digestion products; (3) measurement of increase of amino-nitrogen by van Slyke's method; (4) titration of the acidity of the digestion products; (5) the increase of electrical conductivity; (6) the polariscopic method; (7) colorimetric measurements in the biuret reaction; and (8) in the ninhydrin reaction. The enzymes used were commercial samples of pepsin and trypsin, and the proteins of egg-albumin or casein.

In general, methods (2) or (3) or both appear to be more delicate as a means of detecting proteolysis than either methods (7) or (8), and more delicate, accurate, and generally applicable as a means of measurement than any of the other methods studied.

It is essential in quantitative comparisons so to limit the amount of enzyme preparation used and the time of action as to keep within the region in which the velocity of hydrolysis is directly proportional to the enzyme concentration. The most suitable time is half an hour to one hour.
W. G.

Influence of Carbohydrates on the Accuracy of the Van Slyke Method in the Hydrolysis of Caseinogen. E. B. HART and BARNETT SURE (*J. Biol. Chem.*, 1916, **28**, 241—249).—The Van Slyke method (A., 1911, ii, 944) for the estimation of certain amino-acids or groups of amino-acids in protein was employed by him for the analysis of pure proteins. Later workers have applied the same method directly to such materials as cattle foods containing carbohydrates and fats, as well as proteins. The authors now show that when the method is applied to a mixture of caseinogen and various carbohydrates, the amounts of the different amino-acids obtained vary according to the particular carbohydrates contained in the mixtures. This variation is specially apparent in the hexone bases and non-amino-nitrogen. The direct application of the Van Slyke method to cattle foods affords therefore inaccurate results (compare Roxas, A., 1916, i, 797).
H. W. B.

The Alcohol Test for Milk. I. M. KOLTHOFF (*Pharm. Weekblad*, 1916, **53**, 1589—1599).—The author finds that the action of the alcohol test for milk is dependent on the presence of calcium ions, and that the method is of hygienic and pathological-chemical importance.
A. J. W.

Technique of the Diazo- and Urochromogen-reactions. ZUCKER and RUGE (*Chem. Zentr.*, 1916, ii, 352—353; from *Münch. Med. Woch.*, 1916, **63**, 918).—The following method of performing the Ehrlich diazo-reaction is recommended: 10 c.c. of solution I [sulphanilic acid (5 grams) and hydrochloric acid (D 1·19, 50 grams) in water (1000 c.c.)] are mixed with four drops of solution II [sodium nitrate (0·5 gram) in water (100 c.c.)], 10 c.c. of urine are added, and 3 c.c. of 25% ammonia; if the froth becomes pink on shaking, a positive reaction is indicated. For the urochromogen reaction, the clear urine (10 c.c.) is diluted until colourless, and the dilute urine placed in two similar test-tubes. Five drops of potassium permanganate solution (1:1000) are added to one tube with stirring, and, after half a minute, the colours of the two tubes are compared by daylight. A distinct, canary-yellow coloration of the urine treated with permanganate shows a positive reaction; a pink coloration shows that the urine is too greatly diluted. If the coloration is at first yellow, but disappears after a minute, the reaction is negative; in cases of positive reaction, the intensity of the yellow coloration increases. H. W.

The Absorption of Organic Dyes by Colloidal Soils, Clays, etc. WILHELM GRAF ZU LEININGEN (*Kolloid Zeitsch.*, 1916, **19**, 165—172).—Comparative experiments with various dyes have shown that methylene-blue is the most suitable for use in the investigation of different soils. The assumption that dyes are rapidly absorbed is not in agreement with the author's experience, according to which the process is not complete until after the lapse of several months.

The application of dye absorption in the analysis of soils is critically discussed in reference to the results of experiments, which show that the absorption bears no simple relation to the colloid substances present in the soil. H. M. D.

General and Physical Chemistry.

Spectrographic Studies of some Portuguese Uranium and Zirconium Minerals. A. Pereira-Forjaz (*Compt. rend.*, 1917, **164**, 102—103).—From the spectrographic examinations of specimens of chalcolite from Sabugal and Nellas, autunite from Nellas, and of zircon from the syenite with riebeckite from Alter Pedroso, the elements present in these minerals are given. It is found that carnotite accompanies autunite and chalcolite in the radio-uraniferous district of Portugal, and other uranium minerals also occur with these two, namely, walpurgite, trögerite, and zeunerite. The radium ray $\lambda = 4682{\cdot}4$ is more sensitive than the more intense ray $\lambda = 3814{\cdot}6$. The zirconium ray $\lambda = 4739{\cdot}5$ does not appear to be very sensitive. W. G.

The Circular Polarisation Produced by the Spherolites with Helicoidal Winding. Paul Gaubert (*Ann. Physique*, 1916, [ix], **6**, 356—364).—A more detailed account of work already published (compare A., 1916, ii, 604). W. G.

Inner Mechanism of the Reaction of the Photochemical Oxidation of Hydrogen Iodide. N. P. Strachov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 824—837).—According to Plotnikov ("Kinetics of Photochemical Reactions," Moscow, 1908), the oxidation of hydrogen iodide in aqueous solution by oxygen under the influence of sunlight proceeds according to the scheme:

$$d(O_2)/dt = kJ(KI)^{2/3}(HCl)^{2/3}(O_2),$$

and if the potassium iodide and hydrogen chloride are taken in excess in relation to the oxygen, the reaction is of the first order. At first glance, the light-sensitive component in this case would appear to be the iodine atom in the hydrogen iodide molecule. With this view, certain peculiarities of the reaction are not in accord, especially its insensitiveness to the free iodine formed, which, as it absorbs the active blue and violet light, should play the part of a light-filter. The theory of the reaction was also developed by Plotnikov ("Investigation of Photochemical Phenomena," II, Moscow, 1915), who, on the assumption that the photochemical component is the colourless iodine ion, which should absorb blue light to an infinitely slight extent, derived the equation $dx/dt = kJ_0 i a^{2/3}(b-x)$, where $(a-x)$ and $(b-x)$ are the concentrations of the hydrogen iodide and oxygen respectively, J_0 the intensity of the light impinging on the reacting mixture, i the natural coefficient of absorption for blue light, and k the velocity constant. The iodine formed, giving rise to yellowish-brown compounds, may be expected to retard the reaction, so that the equation becomes modified to $dx/dt = kJ_0 e^{-i_2 px} . a^{2/3}(b-x)$, where i_2 is the coefficient of absorption of blue light by the iodine solution formed and p the thickness of the reacting layer.

That iodine does exert such a retarding influence is shown by interposing iodine solution between the source of light and the reacting mixture. When, however, the effect of iodine acting as an "internal" light-filter is investigated, different results are obtained. Between the limits of concentration, 2·7 and 27 millinormal, iodine exhibits no retarding action, although a solution of the latter concentration completely stops the reaction when used as an "external" light-filter. When, however, the concentration of the iodine reaches the value 54 millinormal, a rapid fall occurs in the velocity constant, the rate of fall being gradually diminished with further increase in the concentration of the iodine. The diminution in the value of the velocity constant is therefore not related simply to the concentration of the iodine. It is pointed out that, owing to change in the iodine complexes, iodine solutions do not conform to Beer's Law.

This disagreement between the observed retardation of the reaction and that assumed by Plotnikov is explained by the author on the supposition that one of the iodine complexes formed is a photochemical autocatalyst, and that such complex is only slightly sensitive to light. This supposition leads to an equation of the first order with respect to $(b-x)$, the concentration of the oxygen.

T. H. P.

Thermo-electric Properties of Certain Polymorphous Metals. P. N. Laschtschenko, S. F. Bykov, and S. V. Efremov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 279—296).—Measurements have been made at different temperatures of the thermo-potentials of a number of pairs of metals, one metal in each case being capable of existing in polymorphous modifications; the numerical results are given, and also the curves showing the connexion between electromotive force and temperature.

The nickel–platinum curve shows a characteristic bend in its early part, but no break, and the temperature-coefficient of the thermoelectric force $(\partial E/\partial t)$ exhibits a minimum at about 400°. With iron–platinum, $\partial E/\partial t$ has minima at 475° and 1025°, and a maximum at 850°, the last temperature corresponding nearly with the transformation of β- into γ-iron (compare Broniewski, A., 1913, ii, 288).

With zinc–platinum, zinc–palladium, zinc–gold, and zinc–iron, the results obtained bear little relation to allotropic change of the zinc. With zinc–copper, however, this change is sharply shown, the neutral point, at which the thermoelectric force is a maximum, being at about 240°; at 310°, the curve again assumes its regular parabolic form, this temperature being regarded as that of the transformation of the zinc. The tin–platinum curve shows no peculiarity, but the tin–nickel curve consists of two branches meeting at a very slight angle at 160—165° (compare Degens, A., 1909, ii, 888; Werner, A., 1913, ii, 1057). The influence of the allotropy of thallium on the thermoelectric properties of the metal appears, from a study of thallium–platinum, thallium–copper, and thallium–nickel, to be only slight (compare Werner, *loc. cit.*).

Investigation has been made of aluminium paired with platinum, palladium, silver, and constantan, the aluminium employed containing 1·30% Si, 0·85% Fe, and traces of copper. In all these cases, the curves exhibit changes in direction at temperatures lying within the limits 570—590°, which are in agreement with those observed by other investigators in other ways. T. H. P.

Electrolytic Dissociation of Individual Salts. A. N. Sachanov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 341—361. Compare A., 1915, ii, 729, 730).—The author's previous work on the electrical conductivity of silver nitrate in solution in different solvents indicates that, even in absence of solvent, this salt exhibits electrolytic dissociation, and in the present paper the consequences of this result, and its bearing on the conclusions drawn by various investigators, are discussed.

It may be regarded as an established fact (compare Foussereau, A., 1886, 844, 975; Poincaré, A., 1889, 457; 1890, 551) that the degree of dissociation of fused binary salts depends not at all or but slightly on the temperature, the diminution in conductivity of the fused salts with fall of temperature being the result only of the increased viscosity, and consequent diminished ionic velocity. The conclusion is therefore drawn that if such fused salt were under-cooled to a low temperature, for instance, 25°, its degree of dissociation would be of the same order as with the ordinary fused condition (compare Walden, A., 1914, ii, 330). The inaccuracy of the view that the dissociation of fused salts is due largely to their high temperatures is pointed out (compare Noyes, "The Electrical Conductivity of Aqueous Solutions," Washington, 1907).

With the change from the fused to the solid state, the electrical conductivity of a salt, such as silver nitrate, diminishes enormously, and such diminution may be due to diminution of either the electrolytic dissociation of the salt or the mobility of the ions. In order to decide between these two alternatives, the author makes use of a cell containing two silver electrodes immersed in silver nitrate, of which the portions in contact with the two electrodes may be kept at different temperatures. It is found possible to keep the silver nitrate in contact with one electrode in the fused, and that in contact with the other electrode in the crystalline condition, the temperatures in the two cases being the same; repeated measurements show that, under such conditions, the electromotive force of this cell is zero (compare Negbaur, *Ann. Phys. Chem.*, 1892, [ii], **47**, 27). From this result, the conclusion is drawn that the concentrations of the silver ions in fused and crystalline silver nitrate at the melting point are identical, the sharp fall in the specific conductivity of the fused salt on crystallisation being due to the diminished ionic velocity. It follows, then, that crystalline binary salts (normal electrolytes) are dissociated electrolytically to approximately the same extent as in the fused state, and it may reasonably be assumed that the degree of this dissociation depends but little on the temperature (compare

R. Lorenz, "Elektrolyse geschmolzener Salze," III, 289; Tubandt and E. Lorenz, A., 1914, ii, 516).

It follows, further, that the current view that salts are resolved into ions on solution is invalid, dissolution only changing the degree of dissociation of indivdual salts to an extent depending on the dielectric properties of the solvent and on such change, usually comparatively inconsiderable, in the electro-affinities of the ions as is caused by possible solvation processes. The idea of the dissociating capacities of solvents as the cause of dissociation of salts also appears quite superfluous. Moreover, one of the strongest arguments against the theory of electrolytic dissociation, namely, the absence of any peculiarity attending the dissolution of salts, vanishes entirely.

The above considerations relate solely to normal electrolytes. Such compounds as hydrogen chloride or aluminium chloride, which in the individual state are non-conductors, undergo more profound change on dissolution; indeed, in these cases, the marked thermal effects accompanying dissolution are evidences of reciprocal action between solvent and salt.

If ionic structure determines the chemical properties of substances, it none the less sharply characterises their thermodynamic relations. Compounds possessing such structure are distinguished by marked reactivity in those conditions which thermodynamics represents as possible for different processes. Finally, one of the most important properties of salt-like substances, namely, their ability to form polymerides and complexes, is also a necessary consequence of their polar structure. T. H. P.

Fuel Cells at High Temperatures. EMIL BAUR, AGNES PETERSEN, and G. FÜLLEMANN (*Zeitsch. Elektrochem.*, 1916, **22**, 409—414. Compare A., 1913, ii, 13).—In a previous paper (*loc. cit.*), various fuel cells were described in which the cathode consisted of molten silver which was saturated with oxygen. The present paper describes a series of fuel cells in which the silver cathode is replaced by easily dissociated oxides. The *E.M.F.* of the following combinations has been determined at temperatures ranging from 700° to 1300°: (i) CuO,Cu_2O | electrolyte | C; (ii) PbO,Pb | electrolyte | C; (iii) Fe_3O_4,FeO | electrolyte | CuO,Cu_2O; (iv) FeO,Fe | electrolyte | CuO,Cu_2O;

(v) NiO,Ni | electrolyte | CuO,Cu_2O;

and (vi) PbO,Pb | electrolyte | CuO,Cu_2O. The electrolyte was borax, glass, or porcelain. In the case of the first combination, rather fluctuating values for the *E.M.F.* were found, ranging up to 1·4 volts at 1200°. The lead oxide combination (ii) gave an *E.M.F.* of about 1·0 volt at 1200°. In the third cell, *E.M.F.* values between 0·7 and 0·8 volt were obtained for temperatures between 700° and 960°. The nickel oxide–copper oxide cell gave a value 0·717 volt at 860°, whereas the lead oxide–copper oxide gave a value of 0·44 volt at 990°. The theoretical voltages obtainable from these cells are calculated, and the reasons for any differences discussed. J. F. S.

Oxygen Pressure of some Oxides and the Carbon-Oxygen Cell at High Temperatures. W. D. Treadwell (*Zeitsch. Elektrochem.*, 1916, **22**, 414—421. Compare preceding abstract).—The oxygen pressure of the oxides of copper, lead, nickel, and iron has been deduced from measurements of the potential of these oxides measured against an electrode of molten silver saturated with oxygen. The measurements were carried out at temperatures from 800° to 1193° with electrolytes consisting of molten borax or easily fusible glass mixed with quartz or porcelain. The cells measured were: (i) $Cu_2O,CuO\,|\,\text{electrolyte}\,|\,O_2,Ag$; (ii) $Fe_3O_4,Fe_2O_3\,|\,\text{electrolyte}\,|\,O_2,Ag$; (iii) $Cu,Cu_2O\,|\,\text{electrolyte}\,|\,O_2,Ag$; (iv) $Pb,PbO\,|\,\text{electrolyte}\,|\,O_2,Ag$; (v) $Ni,NiO\,|\,\text{electrolyte}\,|\,O_2,Ag$; (vi) $FeO,Fe_2O_3\,|\,\text{electrolyte}\,|\,O_2,Ag$; (vii) $Fe,FeO\,|\,\text{electrolyte}\,|\,O_2,Ag$; and (viii) $C\,|\,\text{electrolyte}\,|\,O_2,Ag$. At 1000°, the observed potential was: (i) 0·045 volt, which gives a value of Q for the change $Cu_2O+\frac{1}{2}O_2=2CuO$ of 31,200 cal.; (ii) 0·262 volt, giving the Q value 49,500 cal. for the change $2Fe_3O_4+\frac{1}{2}O_2=3Fe_2O_3$; (iii) 0·367 volt, $Q=40{,}200$ cal. for $2Cu+\frac{1}{2}O_2=Cu_2O$; (iv) 0·478 volt, $Q=50{,}400$ cal. for $Pb+\frac{1}{2}O_2=PbO$; (v) 0·855 volt, $Q=61{,}000$ cal. for the change $Ni+\frac{1}{2}O_2=NiO$; (vi) 0·897 volt, $Q=74{,}200$ cal. for the change $3FeO+\frac{1}{2}O_2=Fe_3O_4$; (vii) 1·040 volts, $Q=66{,}600$ cal. for the change $Fe+\frac{1}{2}O_2=FeO$; and (viii) 1·147 volts, $Q=26{,}750$ cal. for $C+\frac{1}{2}O_2=CO$. The potential and thermal values are, in general, in good agreement with the theoretical values and with those found from direct calorimetric determinations. Cupric oxide has an oxygen pressure of 0·21 atmosphere at 1008°, and 1 atm. at 1085°. Ferric oxide has an oxygen pressure of 0·21 atm. at 1322°, and 1 atm. at 1405°. Cuprous oxide has a pressure of 0·21 atm. at 1693°; lead oxide has an oxygen pressure of 0·014 mm. at 1200°. J. F. S.

The Ionisation of Sulphuric Acid and Neutral Potassium Sulphate in Aqueous Solutions of Moderate Concentrations. J. A. Muller (*Bull. Soc. chim.*, 1916, [iv], **19**, 438—441. Compare A., 1913, ii, 115).—By carrying out the electrolysis of solutions of sulphuric acid and potassium sulphate, each solution containing 1 gram-molecule per litre, under conditions such that the amount of the ions liberated at each electrode could be determined, the author shows that, in solutions of the above concentration, sulphuric acid is ionised to $2H^{\cdot}$ and SO_4'', and the potassium sulphate to $2K^{\cdot}$ and SO_4''. W. G.

Some Electrolyses. J. A. Muller (*Bull. Soc. chim.*, 1916, [iv], **19**, 441—444).—If an electrolytic cell is set up, the cathode being in a porous pot containing a molecular solution of sulphuric acid, and immersed in an outer vessel which contains the anode in a molecular solution of potassium hydroxide, on electrolysis the hydrogen liberated exceeds the sum of the hydrogen equivalent to the potassium which has travelled to the cathode and the SO_4'' which has passed to the anode, and the author considers that this is due to the potassium hydroxide being partly ionised to OK'

and H˙. If in the above cell the potassium hydroxide is replaced by hydrochloric acid, the hydrogen liberated at the cathode is in excess of the sum of the hydrogen equivalent to the hydrochloric acid decomposed and the SO_4'' which has migrated to the anode, this being due to the fact that, towards the end of the electrolysis, oxygenated compounds of chlorine, and, finally, free oxygen, are liberated at the anode, with the result that for every atom of oxygen thus set free a molecule of hydrogen is liberated at the cathode. If in a similar cell the anode cell contains a molecular solution of gold chloride, the only gases liberated are hydrogen at the cathode and oxygen, slightly ozonised, at the anode, there being no separation of gold. W. G.

Dependence of Transport Numbers on the Nature of the Solvent. F. Krüger (*Zeitsch. Elektrochem.*, 1916, **22**, 445—446).—A theoretical paper in which it is shown that the product $v\eta = c'$ and $u\eta = c''$, where v and u are the transport velocities of the anion and cation and η the viscosity-coefficient of the solvent. It is therefore held that the transport numbers will tend to the same value in all non-associated solvents, but in the solvents where the molecules are very large, that is, associated solvents, and in all cases where solvates are formed, the transport numbers will have very different values (compare following abstract). J. F. S.

Determination of the Transport Number of the Silver Ion in 0·01*N*-Silver Nitrate Solution in Mixtures of Ethyl Alcohol and Water at 40°. H. Krumreich (*Zeitsch. Elektrochem.*, 1916, **22**, 446—464).—The author has directly determined the transport numbers of 0·01*N*-silver nitrate solution in various alcohol–water mixtures at 40° by the direct Hittorf method. The following values were obtained: in pure water, 0·4820; 10% alcohol, 0·4821; 30% alcohol, 0·4881; 50% alcohol, 0·4586; 70% alcohol, 0·4464; 90% alcohol, 0·4210; and 99·8% alcohol, 0·4100. The concentration cells of various alcohol–water mixtures of 0·01*N*-silver nitrate were measured, and from the *E.M.F.* values obtained the transport numbers of the silver ion were calculated. The results in this case differed from the results of the direct measurements by from −5·0% to +2·6%. The direct method therefore gives the most trustworthy values, although the indirect method may be used as a control and for deciding whether any secondary reactions have occurred during the direct measurement. The author has, contrary to the results of Carrarra (A., 1903, ii, 708), been unable to show that such occur in his experiments, at least to such an extent that they would affect the value of the transport number. The specific conductivity of the various solutions used in this work was determined at 40° (compare preceding abstract). J. F. S.

Anodic Hydrogen Peroxide Formation During the Electrolysis of Malonates. C. Schall (*Zeitsch. Elektrochem.*, 1916, **22**, 422—423).—The author has electrolysed *N*-solutions of normal and acid sodium and potassium malonates at low temperatures.

The solutions were placed, either in an open apparatus or in a closed U-tube, and cooled with solid carbon dioxide and alcohol. The electrolysis took place between platinum electrodes by means of a current of 0·2—0·4 amp. with a terminal potential of 10 volts. After 0·25—0·5 amp. hour had been passed a quantity of the anode liquid was removed and analysed. This gave both the titanic acid and vanadic acid reactions for hydrogen peroxide, the colour in both cases increasing in intensity the lower the temperature and the longer the current had passed. A quantitative analysis indicated amounts of hydrogen peroxide from 5 to 20 mg. per 100 c.c. of anode liquid. Under analogous conditions, potassium succinate, phthalic acid, and sodium phthalate also yielded hydrogen peroxide at the anode. There was no production of hydrogen peroxide in the case of sodium acetate, and in the case of potassium benzoate in acetone–water a brown coloration was produced which made it impossible to test for hydrogen peroxide.

J. F. S.

Influence of Catalyst Poisons on the Photo-electric Sensitiveness of Platinum. F. KRÜGER and E. TAEGE (*Zeitsch. Elektrochem.*, 1915, **21**, 562—569).—The effect of the poisonous gases, hydrogen sulphide, hydrogen cyanide, carbon monoxide, carbon dioxide, and ammonia on the rate of electron discharge from plates of platinum, palladium, brass, nickel, magnetite, and silver, illuminated by a quartz mercury lamp, has been investigated. It is shown that the photoelectric sensitiveness of platinum is greatly reduced by charging it with the catalyst poisons, hydrogen sulphide, hydrogen cyanide, and carbon monoxide. The strongest effect is shown with hydrogen sulphide. In this case the original conditions cannot be regained by repeated washing with air and evacuation, so that in all probability a layer of platinum sulphide has been formed; this has been advanced as a reason for the catalytic poisoning of platinum by hydrogen sulphide. It is uncertain whether a similar state of affairs occurs with the other poisons. In this case, long evacuation or exposure to air causes a recovery of the sensitiveness of the platinum. This recovery would obviously take place more rapidly and be stronger if only a surface adsorption had occurred and if the photoelectric effect is produced from the surface layer. Gases diffuse, however, into the interior of the platinum, and much more so in the case of palladium. The penetrating depth of the photoelectric action is, however, only 3×10^{-6} cm. (Partzsch and Hallwachs, *Ann. Physik*, 1913, [iv], **41**, 247). Hence the actions in the deeper layers demand that the sensitiveness is dependent on the previous history of the platinum. Charging platinum with nitrogen has no effect, which is analogous to the absence of change in the catalytic and electrochemical effects when platinum is charged with nitrogen. Charging with carbon dioxide produces a slight increase in the photoelectric sensitiveness. Ammonia produces an increase in the sensitiveness, which is apparently contrary to what might be expected, since the catalytic activity of platinum in water formation is decreased by ammonia.

It seems, therefore, that in general a high photoelectric sensitiveness is connected with a strong catalytic action. J. F. S.

Variation of the Specific Heat of Gases with the Pressure. SILVIO LUSSANA (*Ann. Physique*, 1916, [ix], **6**, 344—356).—Polemical. A reply to Peczalski (compare A., 1916, ii, 216). W. G.

Relations between Thermal Properties. Molecular Coefficient and Constitution of Organic Compounds. STEFANO PAGLIANI (*Gazzetta*, 1916, **36**, ii, 310—334. Compare A., 1915, ii, 672, 819; 1916, ii, 291).—The investigations made on elements and inorganic compounds are now extended to organic compounds. Since, however, in most cases the values of the specific heats, especially at low temperatures, are unknown, the values of the entropy have not been calculated, but only the changes of the latter with change of state, that is, the quotient of the heat of fusion or vaporisation by the corresponding absolute temperature. Where direct measurements of the latent heats are lacking, the values obtained from cryoscopic and ebullioscopic measurements are employed.

The general rules obeyed are as follows: (1) For the members of a homologous series the variation of the entropy on fusion diminishes as the molecular-coefficient increases, the highest values of this coefficient usually corresponding with the lowest values of such variation; (2) with isomerides, the variation of the entropy on fusion is constant. That irregularities occur is regarded as due to the experimental difficulties attending the determination of the melting point and heat of fusion of organic compounds. It is found, further, that the values of the change of entropy on fusion, especially among the members of a homologous series, follow the order of magnitude of the changes in the specific volume on fusion, the latter measuring the degree of stability of form.

Rule (1) finds an exception in the series: benzene, toluene, xylene, and in derivatives of this series, but this ceases to be an exception if the higher homologues are regarded, not as alkylated benzenes, but as phenylated paraffin hydrocarbons.

In the case of vaporisation, the variation of the entropy also diminishes as the molecular-coefficient increases with the terms of a homologous series. In this case no exception to the general rule is presented by the series of benzene and its homologues or by derivatives of this series. With hydrocarbons belonging to different series and having equal molecular-coefficients, the variations of the entropy on vaporisation differ but little. With compounds containing carbon, hydrogen, and oxygen, and having equal molecular-coefficients, this variation has maximal values for the saturated alcohols, both aliphatic and aromatic, and minimal values for the saturated aliphatic acids. Almost exactly intermediate positions are held by the nearly equal values for esters and ketones.

For those series with which Trouton's law holds, expressions may be deduced of the following general form:

$$r/T = K/M = K/[(12+2)n + 16n_1 + 14n_2 \pm m],$$

where r is the heat of evaporation, T the absolute boiling point, K Trouton's constant, n, n_1, and n_2 the respective numbers of carbon, oxygen, and nitrogen atoms in the molecule, and m a positive or negative whole number. Thus, for the saturated hydrocarbons, $r/T=20/(14n+2)$, the value for methane being 1·250, which is of the same order of magnitude as the values, 1·430 and 1·341, for water and ammonia respectively; since $T=109°$, the heat of evaporation of methane becomes 136·25 (at $-164°$). This method may be applied generally to the calculation of the heat of vaporisation of compounds of any series for which Trouton's constant is known.

The relation deduced by Duclaux (A., 1913, ii, 104) is based on the universal application of Trouton's Law to all substances, simple and compound, mineral and organic. That this law does not exhibit such universal applicability is shown by the fact that compounds of different chemical functions, even when composed of the same elements and having the same molecular-coefficient, present marked differences in the values of the variation of the entropy accompanying change of state.

The values of the heats of vaporisation of various metals obtained by Wehnelt and Musceleanu (A., 1913, ii, 23) lead to values of the variation of entropy on vaporisation which agree satisfactorily with the periodic relation between variation of entropy and atomic-coefficient.

Taken in conjunction with Casale's expression for calculating approximately the boiling points of hydrocarbons of the methane series, the author's results lead to the formula $r/\Sigma(109{\cdot}2/n^a)$, for the variation of the entropy of a hydrocarbon on evaporation, n being the number of carbon atoms in the molecule. Since for isomerides the variation of the entropy is constant, it follows that the heats of evaporation of isomeric hydrocarbons will diminish as the boiling point falls, that is, as the number of hydrogen atoms in the nuclei diminishes and the number of substituent methyl groups increases.

The total heat of evaporation, being equal to the sum of the external and internal heats, may be expressed by the relation $r=Aup+1{\cdot}9878CT/M\,.\,\ln\,.\,(d/D)$, where A is the thermal equivalent of unit work, u the differential volume between vapour and liquid, p the pressure, C a constant for each substance, T the absolute temperature, D the density of the saturated vapour, and d the density of the liquid. Replacing D by $0{\cdot}08955M/2{\cdot}016$, the variation of the entropy may be expressed by $r/T=Aup/T+1{\cdot}9878C/M\,.\,\ln(d/0{\cdot}04477M)$. Since, for isomerides, the molecular volumes in the liquid state are equal (Kopp), the Dieterici constants at the boiling point exhibit close agreement, and the values of r/T are also equal, the conclusion is drawn that the values of u/T are constant for isomerides at constant pressure; in other words, the increase in volume on vaporisation of isomeric compounds is proportional to the absolute temperature of evaporation. Further, since the molecules are uniformly distributed and their number does not vary, the increase in volume on evaporation, representing the increase of distance between the molecules, is, at any rate for isomeric compounds, proportional to the absolute boiling point. Consequently, as has been previously found, the heats of evaporation of isomerides are proportional to the absolute boiling points.

Of twenty-one organic compounds for which the heats of fusion and evaporation are known, only three or four obey approximately de Forcrand's expression (A., 1903, ii, 267, 353, 409, 466), the so-called constant varying from 20·7 to 40 (compare A., 1916, ii, 291; also Massol and Faucon, A., 1909, ii, 791; 1911, ii, 852).

T. H. P.

Mixtures. FÉLIX MICHAUD (*Ann. Physique*, 1916, [ix], **6**, 223—344).—In the first part of the paper, which is mathematical, the author deduces certain theorems governing the laws of mixtures. From the energy point of view, entropy may be considered as an independent constituent, for which semi-permeable walls can be imagined, and it is capable of exercising an osmotic pressure, this osmotic pressure being a measure of the thermodynamic potential. He then puts forward a theorem by means of which it is possible, without any intermediate calculation, to ascribe to any given thermodynamic system a simple system of equations in which each phase is represented by an equation, each component being represented by a single term in each equation. This theorem permits of the reconstruction, in a simple and rapid manner, of the principal results of the thermodynamics of mixtures (Clapeyron's equation, law of mass action, etc.). A generalised Clapeyron equation may be deduced which contains other formulæ previously considered as distinct. The demonstration of the fact that a monatomic gas is necessarily an inert gas results immediately from this method of considering the subject. One entirely new fact to which this mode of calculation leads is the theorem of solid substances in excess. Thus, in a system comprising a liquid phase, which contains volatile and non-volatile components, suppose that there exists, in addition, a gaseous phase, formed entirely of the volatile components of the liquid phase, and that the non-volatile components are dissolved to saturation in the liquid phase and form each, in the pure state, a solid phase, then, in the equation relative to the liquid phase, the terms relative to the non-volatile components can be neglected.

In the experimental portion of the paper an account is given of a systematic study of the different methods by which the vapour pressure of a mixture can be measured, and the mixed vapour analysed. The two processes are best carried out separately in two distinct pieces of apparatus. The first apparatus, which is a pressure gauge with eleven tubes, permits of the construction, at one experiment and quite accurately, of the total vapour-pressure curve of a mixture of volatile liquids. The mixtures studied were ether–carbon disulphide, and the same saturated with (*a*) picric acid, (*b*) naphthalene, (*c*) camphor; formaldehyde–carbon disulphide, and the same saturated with (*a*) picric acid, (*b*) naphthalene; acetone–carbon disulphide, and the same saturated with (*a*) picric acid, (*b*) acetanilide; ether–chloroform, and the same saturated with (*a*) picric acid, (*b*) acetanilide, (*c*) naphthalene. The results are set out in detail and the curves figured, and they verify the theorem of solid substances in excess, and also lead to the result that the presence of a substance dissolved to saturation tends to make the curve of total pressure more nearly rectilinear. W. G.

Use of Shukov's Apparatus for Molecular Weight Determinations. GEORG VON KOZICKI and ST. VON PILAT (*Zeitsch. angew. Chem.*, 1916, **29**, i, 423—424).—Shukov's apparatus can be used for the determination of molecular weights of dissolved substances when a solvent of relatively high freezing point is used. The method of carrying out the determinations is similar to that used, with the same apparatus, for the determination of freezing points; a Beckmann thermometer cannot be utilised.

The results obtained with ten different solutes, using naphthalene as solvent, are given, and are very satisfactory. T. S. P.

Calorimetry by Combustions with Sodium Peroxide. W. G. MIXTER (*Amer. J. Sci.*, 1917, [iv], **43**, 27—34).—An account is given of the apparatus and of the manipulation involved in the use of sodium peroxide as an oxidising agent in thermochemical determinations. H. M. D.

Physico - chemical Force of Attraction. III. L. G. GURVITSCH (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 856—861. Compare A., 1914, ii, 435; 1915, ii, 744).—The phenomenon of the autodisintegration of floridin which occurs in various liquids necessitates the assumption that the force of physico-chemical attraction which tears off small particles from the surfaces of the floridin granules is capable of similar behaviour at the surface of other substances, such as metals. Experiment shows, indeed, that metals do undergo pulverisation when shaken in the form of granules or small pieces with various liquids at the ordinary temperature. Between the degree of disintegration of the metal and the residual chemical energy of the liquid, measured by the heat of adsorption, perfect parallelism exists, and the conclusion is drawn that the pulverisation is caused by the physico-chemical force of attraction between metal and liquid. This force is alone insufficient to tear particles from the compact surface of the metal, but becomes able to do so when the impacts of the metallic fragments loosen the surface layers.

The shaking of certain liquids of specially great residual energy, such as water, methyl alcohol, acetone, etc., with metals may even lead to the formation of colloidal solutions of the metals of very considerable concentration and marked stability. The maximal percentage concentrations of the colloidal solutions obtainable on shaking 100 grams of granulated lead with 120—130 c.c. of various liquids are: water, 0·098; methyl alcohol, 0·132; ethyl alcohol, 0·0134; amyl alcohol, traces; acetone, 0·0115; pinene, 0·0088; and aniline, 0·0071. In methyl alcohol, colloidal solutions of the following percentage concentrations are obtainable: cadmium, 0·052; zinc, 0·0028; bismuth, 0·059; mercury, 0·032; and tin, 0·0031.

This procedure furnishes a very simple method for obtaining colloidal metal solutions, but it is attended with some uncertainty, which appears to be due to insufficient cleanness of the surface of the vessel in which the shaking takes place. The best results are obtained if the vessel is washed successively with chromic–sulphuric acid mixture, water, alcohol, and several times with the liquid to be employed; it should then be charged at once and closed. Excessive shaking may result in the complete deposition of the metal from the colloidal solution. T. H. P.

Surface-tension Tables from Data by Traube and Forch. R. Somogyi (*Int. Zeitsch. physikal.-chem. Biol.*, 1916, **3**, 60—70).—The tables give the densities and capillary constants of various alcohols, aldehydes, acids, bases, salts, etc. H. W. B.

Influence of the Quantity of the Adsorbent, Aluminium Hydroxide, on the Adsorption of Aqueous Solutions of Hen's Egg-albumin of Constant Concentration. M. A. Rakuzin and (Mlle.) Ek. Maks. Braudo (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 461—465).—The adsorption of egg-albumin in 7·05% solution by proportions of dry, commercial, precipitated aluminium hydroxide varying from 15% to 1·875% of the weight of the solution has been investigated. When the proportion of adsorbent is below a certain minimum, no adsorption takes place, but increase of the adsorbent to 13% is then accompanied by rapid increase in the percentage of the total albumin adsorbed to a maximum of about 20%. The latter value is not increased by addition of a further quantity of adsorbent to the solution.

T. H. P.

Protein Substances and Anti-substances as Products of Adsorption. M. A. Rakuzin (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 465—468).—From analogy with the separation into toxin and anti-toxin occurring when anti-diphtheritic and other serums are treated with adsorbents (compare Ostromisslenski, A., 1915, i, 751, 752; Zunz, *Zeitsch. Immunitätsf.*, 1914, 326), the author regards the separative adsorption of proteins, enzymes, etc., by aluminium hydroxide as separation into an adsorbed portion and a non-adsorbed anti-substance. Thus, hen's egg-albumin, $[\alpha]_D -37{\cdot}1°$, yields 19·22% of adsorbed albumin I, $[\alpha]_D -56{\cdot}0°$, and 80·78% of "anti-albumin," $[\alpha]_D -32{\cdot}6°$; hen's egg-albumin peptone, $[\alpha]_D -95{\cdot}24°$, gives 24·19% of adsorbed peptone I, $[\alpha]_D -156{\cdot}68°$, and 75·81% of "anti-peptone," $[\alpha]_D -75{\cdot}0°$; and diastase (optically inactive) yields 7·10% of adsorbed diastase I and 92·90% of "anti-diastase," the latter, but not the former, giving Ostromisslenski's reaction with picramic acid. In the case of the solid paraffins of Grosny naphtha, adsorption effects removal of the lower homologues present, and it may be assumed that the adsorbed fractions of proteins, enzymes, and serums are also of lower molecular weight than the non-adsorbed fractions remaining in solution.

T. H. P.

Retarded Diffusion and Rhythmic Precipitation. J. STANSFIELD (*Amer. J. Sci.*, 1917, [iv], **43**, 1—26).—An account is given of earlier work on the formation of rhythmic precipitates, and further experiments are described in which the author has investigated more particularly the phenomena associated with the precipitation of silver chromate by diffusion of silver nitrate and potassium chromate, when one of the reagents is in the form of an aqueous solution and the other in the form of a gelatin jelly.

The results obtained show that separated bands of precipitate are most readily produced when a concentrated silver nitrate solution diffuses into a weak chromate solution. The diffusion of a strong chromate solution into a weak silver solution yields similar results, but the particles formed are larger. When the concentrations of the two reagents approximate to equality, the precipitate appears to be continuous, but under the microscope it is seen to be finely banded.

The gradual increase in the distance between the bands during the process of rhythmic precipitation has been attributed to progressive dilution, but it seems that the rate of diffusion is an important factor. The rates of diffusion of different substances in gelatin vary considerably, and a strong solution diffuses more rapidly than a weak solution. The rate of diffusion of a given aqueous solution is retarded by increasing the concentration of the jelly, and the total range of diffusion is also diminished by this increase in the jelly concentration. H. M. D.

Molecular Condition of Pure Liquids. P. N. PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1008—1032).—The author develops methods of investigating the molecular state of liquids and saturated vapours based on the properties of the thermodynamic functions, and the principles of the theory of corresponding states, independently of any particular form of the equation of state.

Proof is advanced of the following so-called "capillary–chemical law of equimolecular surfaces": With all normal liquids forming, at corresponding temperatures, disperse systems with equimolecular surfaces (systems of equimolecular degrees of dispersion), the free molar surface energies are proportional at corresponding temperatures. This relation may be expressed conveniently in the form $(\gamma v^n/T)$(corres.)$=$a universal constant$=c$, γ being the surface tension, v the molecular volume (M/d), n an arbitrary number, and T the absolute temperature; for corresponding values of T, the values of c for different liquids should be dependent, not on the chemical nature of the compound, but only on the temperature. Introduction of different values for n into this equation leads to a number of universal constants, c_0, c, c_1, c_2, etc., and normal liquids should satisfy each of the relations thus obtained.

Further, $d(\gamma v^n)/dT=k$, that is, the thermal coefficient of the molecular free surface energy for all disperse drops of a system with equimolecular surfaces, is constant, independently of the chemical nature of the substance. Integration of this expression within the limits from the critical temperature to a temperature very near to it leads, on the assumption that $\gamma=0$ at the critical temperature, to the equation $\gamma v^n/(T_c-T)=A$, A being also a universal constant, independent of the chemical nature of the compound, but dependent on the temperature. Substitution for n of the values 0, 2/3, 1, 2, etc., gives expressions for a series of universal constants, A_0, A, A_1, etc., each of which should be satisfied by normal liquids.

Investigation of the values of the functions $\gamma v^n/T$ and $\gamma v^n/(T_c-T)$ for a number of liquids shows that the following liquids are abnormal: (1) *n*-octane, *m*-xylene, mesitylene, durene, naphthalene, diphenylmethane, αβ-dibromoethane; (2) methylaniline, dimethylaniline, acetonitrile, propionitrile; (3) acetone, anisole, and phenetole; (4) water, methyl, ethyl, propyl, *n*-butyl, *iso*butyl, and *iso*amyl alcohols; (5) acetic, propionic, *n*-butyric, *iso*butyric, and *iso*valeric acids; (6) methyl acetate, methyl and ethyl propionates, methyl butyrate and *iso*butyrate; (7) bromine, nitrogen tetroxide, carbon disulphide, and silicon tetrachloride. Ethyl ether and carbon tetrachloride are normal liquids, as also is propyl formate in the temperature interval 0·6054—0·8464.

T. H. P.

Relation between the Physical Properties of Solutions and their Mixtures. ERIK ANDERSSON (*Medd. Nobel Inst.*, 1916, **3**, No. 12, 1—22).—It is shown that the mixture rule is applicable to mixtures of solutions of different electrolytes containing a common ion, and that the calculated values of the density, electrical conductivity, surface tension, coefficient of expansion, and freezing-point depression are in close agreement with those found by experiment. The mixture rule is also applicable in respect of the density when solutions of sucrose are mixed with various salt solutions, but such mixtures do not satisfy the mixture rule in respect of the freezing-point depression.

H. M. D.

Structure of True Solutions and Nature of the Transformations Occurring in Them. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 532—537).—In this communication, the following points, to be dealt with in detail later, are briefly considered.

When solutions (about 1%) of oleates of various metals in xylene are heated from the ordinary temperature to the boiling point, the following changes of colour occur: nickel oleate, green $\rightleftarrows$ greenish-yellow $\rightleftarrows$ yellow (b. p.); chromium, violet $\rightleftarrows$ green; iron, orange $\rightleftarrows$ orange-red; cobalt, red $\rightleftarrows$ violet $\rightleftarrows$ lilac $\rightleftarrows$ blue $\rightleftarrows$ indigo (b. p.); these colour changes occur suddenly as the temperature changes, and are perfectly reversible. Similar series of colour changes are produced in aqueous solutions of the chlorides of the same metals either by heating or by saturation with hydrogen chloride, but most of the theories advanced to explain this phenomenon, for instance, those based on the assumption of hydration or ionisation, are inapplicable to solutions of anhydrous oleates in completely anhydrous aromatic hydrocarbons.

According to the author's theory, such colour changes in true solutions are due to changes in the magnitude of the intensity factor of the volume energy of the molecules, that is, of their condensation, which is often accompanied by reactions of combination or decomposition. The change in this intensity factor may be caused by different kinds of energy, for instance, thermal, volume (great contraction) or chemical (solvation, desolvation, solventolysis, hydrolysis, and the like) energy, and identical changes in the intensity factor of the volume energy of the molecules exert identical effects on the absorption of light energy by the solutions, quite independently of the kind of energy causing the changes.

Complete parallelism exists between the colours of dispersoid solutions of the chlorides, and their hydrates and hydrochlorides, of copper, nickel, cobalt, iron, and chromium in aromatic hydrocarbons, and those of true solutions in the same compounds. From the experimental data obtained, the following conclusions are drawn: (1) True solutions undoubtedly possess a granular structure, that is, are disperse, their stability being due to causes given in the author's dispersoidological theory of true solutions (A., 1913, ii, 678). (2) Investigation of dispersoid solutions of coloured salts represents a powerful agent for the elucidation of the nature of true solutions, and permits of the determination of the chemical or physical transformations responsible for the changes in colour.

The weaker the base combined with oleic acid in an oleate, the more readily soluble is the oleate in aromatic hydrocarbons, and the more nearly does the solution obtained approach typical true solutions, both in degree of dispersiveness and in other properties. In other words, in an oleate containing a weak base, the property of oleic acid of dissolving (and solvating) in aromatic hydrocarbons is weakened to a less extent than in an oleate containing a stronger base (compare A., 1916, ii, 177).

The bearing of these considerations on the causes underlying the solubility and insolubility of substances is discussed.

T. H. P.

The Actual State of the Theory of Electrolytic Dissociation in Water and Non-aqueous Solvents. BOHDAN DE SZYSZKOWSKI (*Medd. Nobel Inst.*, 1916, 3, No. 11, 1—16).—The formula proposed by the author (A., 1915, ii, 616) to express the relation between the degree of ionisation and the concentration of an electrolyte is shown to be equivalent to the formula put forward by Kraus and Bray (A., 1913, ii, 914). In the latter, however, the deviation from the law of mass action is attributed to the influence of the ions, whilst the author's formula,

$$c\alpha^2/(1-\alpha)=K+k(c_0^{1/3})^m,$$

ascribes the deviation to the influence of the undissociated molecules, the concentration of which is given by $c_0=c(1-\alpha)$.

Analysis of the equation leads to the conclusion that the existence of a minimum value of α requires that the constant K should be comparatively large, this minimum being the resultant of the effect produced by the operation of the law of mass action as measured by K and that produced by the action of the undissociated molecules as measured by $k(c_0^{1/3})^m$.

From an examination of the data recorded by Kraus and Bray for non-aqueous solutions, it is found that the product of the constant m and the specific inductive capacity ϵ has approximately the same value for all solvents. According to Walden, the linear concentration $c^{1/3}$, corresponding with the minimum value of the degree of ionisation, is also related to the specific inductive capacity of the solvent in accordance with the equation $\epsilon/c^{1/3}=$constant, and by continuing these relations the author arrives at the equation $m \,.\, c^{1/3}=$constant. In other words, the constant m in the above ionisation formula varies inversely as the distance between the molecules of the electrolyte in the solution, which shows a minimum conductivity.

Although Kraus and Bray have assumed that the ionisation curve on both sides of the minimum is represented by the above equation, the actual observations seem to show that a more complex expression is required to give a complete account of the ionisation relations. This may be done by an equation of the type $c\alpha^2/(1-\alpha)=k_m(c_0^{1/3})^m+k_n(c_0^{1/3})^n+K$, in which $m>3$ and $n<3>0$. In this equation, the first term determines the behaviour of the electrolyte in concentrated solution, whilst the second and third terms regulate the behaviour in dilute solution. This equation, in combination with $m\epsilon=$constant, leads to the conclusion that the concentration of the solution at which the minimum conductivity occurs is the greater the greater the specific inductive capacity of the solvent. H. M. D.

Influence of Electrolytes on the Dissociating Power of Solvents. III. A. N. Sachanov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 361—372. Compare A., 1914, ii, 419; 1915, ii, 526, 732). —Cryoscopic measurements on solutions of dimethylpyrone and hexachloroethane in aniline give for the latter the cryoscopic constant 63·5—63·8, the value calculated from the latent heat of fusion being 67·5. The low value obtained by Ampola and Rimatori, namely, 58·7 (A., 1897, ii, 306), is due to the formation of complexes.

The molecular weights of pyridine and aniline in acetic acid, as determined cryoscopically, are comparatively little above the normal values, although the increase of the molecular weight with the concentration, particularly for aniline, is clearly marked.

According to the hypothesis which assumes the formation of complexes able to conduct, a normal magnitude of the coefficient i or of the molecular weight on abnormal dissociation is indicative of marked electrolytic dissociation of polymeric molecules. Further, this hypothesis leads to the conclusion that the freezing-point depression of a mixture of two electrolytes, possessing on abnormal dissociation normal molecular weights, should be the sum of the two partial depressions of the separate electrolytes. Actual experiment shows that the depression of a mixture of pyridine and aniline acetates in acetic acid is, within the limits of experimental error, additive; only for quite concentrated solutions is the measured depression a little greater than the calculated value, probably owing to solvation. The molecular weight of potassium formate in acetic acid is considerably less than the normal value, the formic acid being replaced by acetic acid in the salt; the extent to which this replacement proceeds increases with the dilution of the salt, so that in dilute solutions the molecular weight is approximately one-half of the calculated value. Only one mixture of potassium formate and pyridine acetate in acetic acid was examined, additivity of the partial depressions being observed.

These results support the formation of conducting complexes, and are in contradiction to the hypothesis which assumes a dissociating influence of the ions on neutral molecules. T. H. P.

The Phenomena of Suspended Transformation. GERTRUD KORNFELD (*Monatsh.*, 1916, **37**, 609—633).—After reviewing the arguments for and against the existence of a metastable region for supercooled liquids and supersaturated solutions, in which crystallisation will not occur spontaneously, but needs the presence of a suitable nucleus, the result is given of a large number of experiments on the crystallisation of salol in sealed glass tubes at 25° and 30°. As a result of the investigation, the conclusion is drawn that, in the majority of the tests made, crystallisation occurred spontaneously, the influence of impurities being evident only in a very small proportion. At the temperatures used, gentle agitation is insufficient to induce crystallisation, so that the observations do not favour the idea of a metastable region, and appear to confirm the views of Pfaundler (this Journal, 1877, i, 433, 435) and de Coppet (this Journal, 1876, i, 184) of spontaneous crystallisation as dependent on kinetic molecular conditions. D. F. T.

The Existence, Size, and Determination of Crystal Molecules. A. FOCK (*Centr. Min.*, 1916, 392—396).—The author argues in favour of the existence of chemical molecules as such in crystals, as opposed to the theory, supported by *X*-ray analysis, that atoms or electrons are situated at the points of the point-systems in crystal structures. L. J. S.

Table of Schoenflies's Cubic Space-lattices. PAUL NIGGLI (*Centr. Min.*, 1916, 497—505).—Schoenflies's thirty-six space-lattices are reduced to nine types of point-systems and are represented in a table. Examples are given of how various cubic substances conform with these structures when the atoms or ions (groups of atoms as suggested by *X*-ray analysis) are situated at the points of these point-systems. L. J. S.

Theory of Peptisation. WILDER D. BANCROFT (*J. Physical Chem.*, 1916, **20**, 85—117).—A theoretical paper, in which peptisation is critically considered. Accepting Freundlich's generalisation that adsorption involves a lowering of the surface tension of the adsorbing phase, the author puts forward the following as a theory of peptisation. Any substance which is adsorbed by a second will lower the surface tension, and will therefore tend to disintegrate, in other words, to peptise it. Should the Freundlich generalisation prove not to be universally true, such a theory may be easily modified to account for new facts. The theory being accepted, it follows that peptisation may be brought about by a solvent, by a dissolved non-electrolyte, by an ion, by an undissociated salt, and by a colloid. Adsorption decreases in general with rising temperature, and so does the cohesion of the adsorbing substance. Hence peptisation may be brought about by a solvent at high temperature even when it does not occur at low temperatures. As instances of this, the author discusses the cases: glass–water, vulcanised rubber–organic solvents, and gelatin–water. As cases of peptisation by a dissolved non-electrolyte, the author discusses sugar or glycerol and hydroxides in water, and ether and pyroxylin in alcohol. Typical cases of ion peptisation in water are silver bromide and potassium bromide, silica or chromic oxide and potassium hydroxide, alumina and acids, and chromic oxide and chromic chloride. No case of peptisation by a soluble undissociated salt has been studied as such, but if impure mercury is shaken with water, peptisation is brought about by the oxide film. As typical cases of peptisation by a colloid in water, silver bromide–gelatin, alkaline chromic oxide–hydrated ferric oxide, and gold–stannic oxide are quoted and discussed. Since adsorption depends on the surface, and since peptisation involves breaking down the cohesion of particles, there is no necessary connexion between the amount of adsorption and the ease of peptisation. A coarse-grained, porous precipitate may be peptised more readily than the same mass of substance in a more dense form. Von Weimarn's theory of peptisation, which assumes that the solid always dissolves in the peptising agent, forming unstable compounds which then break down the precipitate forming a sol, is discussed and shown to be inadequate. J. F. S.

Viscosity and Hydration of Colloidal Solutions. SVANTE ARRHENIUS (*Medd. Nobel Inst.*, 1916, **3**, No. 13, 1—20).—The fact that the viscosity of many colloidal solutions changes more rapidly than the concentration is not in agreement with Einstein's formula, and Hatschek has expressed the view that this is due to the formation of an envelope of the dispersive medium round each particle of the disperse phase. When the quantities of water associated with the colloidal particles are calculated for various solutions, numbers are obtained which are difficult to reconcile with the chemical relations between the disperse phase and the dispersive medium.

The data for colloidal solutions of sulphur and various proteins have accordingly been re-examined, and it is found that the experimental observations can be simply interpreted in terms of the author's formula for the viscosity of mixtures as modified by Kendall (A., 1914, i, 109). In the case of sulphur sols, the formula may be applied directly with entirely satisfactory results, but for solutions of proteins it is necessary to assume that the molecules are hydrated to some extent. The combined water per gram of protein varies from 0·7 gram for egg-albumin to 2·2 grams for euglobulin. These quantities of water are much smaller than those obtained on the basis of Hatschek's hypothesis.

The fact that this hypothesis leads to the conclusion that the size of the water envelope is approximately proportional to the change in the viscosity produced by the addition of 1 per cent. of protein, is also said to afford internal evidence that it cannot afford a basis for the determination of the degree of hydration of colloids.

H. M. D.

Relation between the Colour and the Degree of Dispersion of Particles in Coloured Solutions. W. HARRISON (*J. Soc. Dyers*, 1917, **33**, 7—9).—A criticism of Ostwald's view (A., 1911, ii, 868) that the colour of colloidal solutions varies with the size of the particles, and changes in the direction yellow—red—blue, with increase in the size of the particles.

If acid is added gradually to a colloidal solution of night-blue free base, it first dissolves with very little change in colour, is then precipitated without colour change, and finally redissolves with change in colour through green to yellow. Similar behaviour is exhibited by Victoria-blue B, Nile-blue, acid-violet 7B, and formyl-violet S4B. These changes are not in accordance with Ostwald's rule.

If the above dyes are dissolved in glacial acetic acid, they change in colour in the direction violet—blue—green—yellow on the addition of mineral acids, but there is no visible change in the size of the particles. The amount of mineral acid required is much less than in aqueous solution.

In the author's opinion, change in colour is more probably due to molecular rearrangement, and not to change in the size of the molecular aggregate, although it is possible that these changes may occur simultaneously. H. M. D.

Protective Colloids. IV. Radix Althaeæ as Protective Colloid. A. GUTBIER and G. L. WEISE (*Kolloid Zeitsch.*, 1916, **19**, 230—234. Compare this vol., ii, 21).—The protective action of extracts of the root of marsh mallow on solutions of colloidal gold, obtained by the reducing action of hydrazine hydrate, pyrogallol, catechol, and tannin, has been examined in detail. The increase in stability of the gold solutions in presence of the protective colloid is much less marked than that found in previous experiments with other plant extracts. H. M. D.

Protective Colloids. VII. Cydonia Seed as Protective Colloid. A. GUTBIER and A. WAGNER (*Kolloid Zeitsch.*, 1916, **19**, 235—241).—The preparation of colloidal solutions by extracting quince seeds with water is described. The stability of the solutions has also been examined, with special reference to the influence of time, concentration, temperature, salts, acids, and alkalis.

H. M. D.

Ultra-microscopic Investigation of Tanning Phenomena in Jellies. W. MOELLER (*Kolloid Zeitsch.*, 1916, **19**, 205—213).—An account is given of the ultra-microscopic structures which are exhibited by gelatin jellies when these are subjected to the action of alcohol, tannin, chromic salts, and formaldehyde. The micro-photographic records show that the phenomena associated with the action of these reagents on jellies are closely similar to those which are characteristic of the tanning of hide fibres. The actual differences are due solely to the circumstance that the fibrils in the hide are orientated, whilst those in the jelly are distributed in all possible directions. It is assumed that gelatin contains two substances, α- and β-gelatin, of which only the α-gelatin forms the structural units, whilst the β-gelatin is structureless and occupies the spaces between the fibrils of α-gelatin. In the jelly these fibrils are independent of one another, and under the influence of external forces, the irregular net-work may be transformed into a system in which the fibrils are orientated, and in this way structures are developed which vary according to the nature of the forces to which the gelatin jelly is subjected. H. M. D.

Internal and Surface Structures in Jellies. I. W. MOELLER (*Kolloid Zeitsch.*, 1916, **19**, 213—219. Compare preceding abstract).—The author has examined the structure of gelatin subjected to the action of water vapour and warm water, of gelatin jellies before and after dehydration, and also the structure of gelatin which has been heated to a temperature at which it begins to decompose or has been subjected to the action of superheated steam and subsequently drawn out into threads.

The observations afford evidence in support of the view that gelatin consists of an irregular conglomerate of fibrils forming a network of α-gelatin with β-gelatin in the intervening spaces. The structure becomes visible when the gelatin is subjected to any action which removes the β-gelatin partly or completely. In these circumstances the fibril units of α-gelatin undergo orientation to a greater or less extent, forming fibril groups which are visible in the ultra-microscope. H. M. D.

Imitation of Certain Anatomical Structures. MARTIN H. FISCHER and MARIAN O. HOOKER (*Kolloid Zeitsch.*, 1916, **19**, 220—230. Compare A., 1916, i, 693; ii, 557).—A description is given of certain morphological structures shown by colloids or mixtures of colloids which have been subjected to hydration or dehydration. Attention is directed to the close resemblance between these and the structure of various forms of differentiated protoplasm in the living organism, and it is suggested that this differentiation of living protoplasm may be brought about by influences similar to those which are found by experiment to produce differences in the structure of simple colloids. H. M. D.

Non-, Uni- and Bi-variant Equilibria. X. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 514—527. Compare A., 1916, ii, 476).—A further discussion of

equilibrium relation in which it is shown that three types of pressure–temperature diagrams may be differentiated.
H. M. D.

The Equilibrium Solid-Liquid-Gas in Binary Systems which Present Mixed Crystals. IV. H. R. Kruyt (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 555—564).—In a previous communication (compare this vol., ii, 81), it was shown that the coexistence of solid, liquid, and vapour in the system in which bromine and iodine are the components was characterised by the pressure–temperature curve showing two maxima and a minimum. In this system, the compound IBr is formed, and this forms mixed crystals with the components, but it is shown that this type of pressure–temperature curve may also be obtained when mixed crystal formation does not occur. H. M. D.

Principle of the Change of an Equilibrated System under the Influence of an External Agent. II. E. Volchonski (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 272—278. Compare A., 1912, ii, 441).—An analytical proof is given of the principle: Within an equilibrated system, subjected to external influence, all the processes which occur, taken either together or singly, are of such sign that they aid the work of the external factor. T. H. P.

Equilibrium between Mucic Acid and its Lactones. W. A. Taylor and S. F. Acree (*J. Physical Chem.*, 1916, **20**, 118—120).—A preliminary paper in which experiments, designed to determine the equilibrium conditions of acid and lactone in aqueous solution, are described. Quantities of mucic acid in excess were placed in water, and heated (*a*) at 30° for an hour, (*b*) at 100° for thirty minutes, and (*c*) kept at the ordinary temperature for some time. The solutions were then placed in a thermostat at 25°, and filtered portions withdrawn at intervals. The free acid was determined by titration in ice-cold solution with standard alkali solution, and the amount of lactone by adding an excess of $N/10$-standard alkali, boiling for a few minutes, and then titrating the excess of alkali with $N/10$-hydrochloric acid. The experiments show that the same equilibrium is reached in all three cases, the cases (*b*) and (*c*) requiring 1440 hours, and (*a*) requiring 2880 hours, on account of supersaturation. At equilibrium, there were roughly twice as many lactone groups as carboxyl groups in the solution. The data are insufficient to indicate whether the lactone present is a monolactone or a dilactone. J. F. S.

Erroneous Interpretation of the Kinetics of Chemical Reactions. A. Gerasimov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 456—457).—If, in a reaction of the first order, A mols. of the reacting substance are taken in V litres of solution, and x mols. undergo change in time t, the velocity of the reaction is expressed by the equation $-d[(A-x)/V]/dt=K(A-x)/V$ (i). When the volume remains constant, this equation gives

$$-1/V.d(A-x)/dt=K(A-x)/V \text{ or } dx/dt=K(A-x) \text{ (ii)}.$$

If, however, the volume is not constant, either because there is an actual change or because the volume occupied by the reacting molecules requires a correction, equation (ii) is inapplicable, equation (i) becoming $dx/dt=(A-x)(K-1/V.dv/dt)$ (iii). Similar relations hold for reactions of higher orders. The author points out that equation (ii) has been erroneously employed by various investigators in cases where the volume varies, and where, consequently, equation (iii) should be used. T. H. P.

Time Reaction of the Neutralisation of Carbonic Acid and the True Dissociation Constant of Carbonic Acid. A. THIEL (*Zeitsch. Elektrochem.*, 1916, **22**, 423—424).—Polemical. The author criticises the work of Pusch (A., 1916, ii, 477, 557), and claims the field of work entered by Pusch as his own. Reference is made to work by the author and Strohecker (A., 1913, ii, 199; 1914, ii, 361, 448), and also by Strohecker (A., 1916, ii, 522).

J. F. S.

Reaction between Amylene and Trichloroacetic Acid in Different Solvents. II. G. E. TIMOFEEV and V. A. KRAVCOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 985—993. Compare A., 1915, ii, 755).—Oxygenated solvents form with trichloroacetic acid more or less stable solvates, and thus play the part of weak bases. In order to ascertain the effect of non-oxygenated basic compounds in this direction, the authors have investigated the change caused in the extent to which the reaction,

$$CCl_3\cdot CO_2H+C_5H_{10} \rightleftharpoons CCl_3\cdot CO_2\cdot C_5H_{11},$$

occurs in the indifferent solvent, benzene, by the presence of dimethylaniline, pyridine, or diphenylamine; the experiments were made at both 25° and 50°.

At either temperature, the reaction is considerably checked by the addition of the first portions of dimethylaniline, the effect being greater than with oxygenated solvents, as would be expected from the higher basicity. As the proportion of added base increases, the curves for 25° and 50° exhibit a distinct tendency to approach and cut, as has already been found for acetone and for methyl ethyl ketone (*loc. cit.*). The effect is very nearly proportional to the proportion of base added, the curves approximating closely to straight lines. Similar results are obtained if the dimethylaniline is replaced by pyridine.

With diphenylamine, different results are yielded. In agreement with the much feebler basicity, the effect is here much less marked than in the previous cases, and the curves are more nearly similar to those of oxygenated solvents. The curves at 25° and 50° are perfectly parallel, the distance between them being about 11%, which is the same as for pure benzene at the same temperatures.

The conclusion is drawn that the amount of the acid falling to the share of the diphenylamine is constant, independently of the temperature, that is, that the complex which the base forms with trichloroacetic acid is stable as regards temperature. T. H. P.

Velocity of Solution of Metals. II. Velocity of Solution of Zinc in Acids. M. Centnerszwer (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 470—524. Compare A., 1915, ii, 562, 563). —A number of further results have been obtained, the principal ones being as follows.

Etched zinc dissolves in hydrochloric acid more rapidly than zinc with a polished surface. The metal, which reaches its maximum velocity of dissolution in $2N$-hydrochloric acid, dissolves in fresh acid with a continually diminishing velocity, and the process of solution follows Boguski's law. Sulphuric acid dissolves zinc appreciably more slowly than does hydrochloric acid with an equal concentration of hydrogen ions.

Zinc sheets from one and the same melt dissolve with different velocities, owing to variations in the crystalline structure of the metal, but with rolled zinc sheets, concordant results are obtained. Zinc which has been treated with emery dissolves more rapidly than polished zinc, and zinc plates subjected to the action of iodine solution more rapidly than fresh plates.

The velocity of dissolution of the metal increases more rapidly than the concentration of the acid, and the black precipitate which forms at the surface of the metal during the action accelerates dissolution, removal of this precipitate resulting in the loss of the former activity of the metal. In distilled water, zinc retains its activity for a long time, but in the air the metal partly loses its activity. When rapidly cooled, zinc exhibits a more pronounced induction period than when slowly cooled, but if its surface is subsequently etched, its velocity of dissolution is the same as in the latter case. Prolonged heating at 400° of zinc which has been rapidly cooled increases its period of induction. The potential of active zinc is somewhat higher than that of passive zinc.

In order to explain the phenomena observed, the supposition is made that ordinary (chemically pure) zinc is in a passive condition, increase of the velocity of dissolution during the period of induction being explained by transformation of the metal from the passive to the active state.

An attempt is made to explain the passivity of iron and other metals in accordance with Helmholtz's theory of the electric double layer, and it is shown that such a representation is capable of furnishing explanations of: the influence of foreign metals on the solution of zinc (De la Rive's theory), the influence of mechanical and chemical treatment of the surface of the zinc, the period of induction, periodic phenomena in the dissolution of metals (Adler's theory, A., 1912, ii, 891), the passivification of metals by means of oxidising agents and polarisation, rusting of iron and other metals (compare Walker, Cederholm, and Bent, A., 1907, ii, 875; Cushman, *Elektrochem. Metallurg. Ind.*, 1907, **5**, 257, 365), the activation of metals by hydrogen (compare Grave, A., 1911, ii, 896), the specific influence of different electrolytes on the condition of metals, etc. T. H. P.

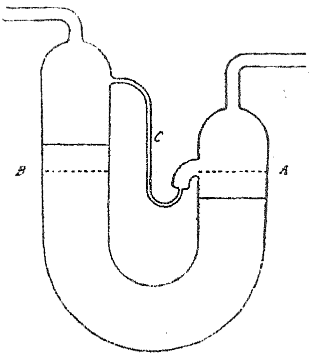
Rhodium Catalysis of Formic Acid. PH. C. WLADISLAW HAAS (*Zeitsch. Elektrochem.*, 1916, **22**, 443—445).—The author is of the opinion that the catalytic activity of the noble metals is to be attributed to electrochemical actions, and to confirm this view the decomposition voltage of formic acid has been determined between electrodes of various types and sizes. A 30% solution of formic acid was used in all experiments; with two bright electrodes, irregular decomposition curves were obtained, but no definite decomposition voltage could be observed. Using two platinised electrodes, the nature of the curves changed, and a definite value of 0·24 volt was obtained for the decomposition voltage. It was also found that if the anode alone was platinised, a definite value could be obtained for the decomposition voltage. Using two platinsed electrodes which were covered with activated rhodium, the author was unable to find any difference in the decomposition voltage (compare Blackadder, A., 1913, ii, 36). J. F. S.

Theory of Heterogeneous Catalysis. L. G. GURVITSCH (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 837—856).—Detailed investigation of the reaction of pinene with floridin (A., 1915, i, 933) leads to the conclusion that the initial products of this reaction are polyterpenes, which, under the influence of the heat developed, subsequently undergo partial decomposition into simple terpenes. The formation of the polyterpenes is caused by the adsorption of the pinene on the surface of the floridin, propinquity of the pinene molecules being thus effected; factors which impede this adsorption also retard the transformation of the pinene.

A catalytic reaction of another type has been discovered in the action on carbon disulphide of the partly dehydrated aluminium hydroxide obtained from metallic aluminium in presence of traces of mercury; this reaction, which proceeds at the ordinary temperature, is expressed by the equation $CS_2 + 2H_2O = 2H_2S + CO_2$. The yield of hydrogen sulphide attains a maximum for a certain percentage of water in the alumina, and the conclusion is drawn that the transformation of the carbon disulphide is a result of its adsorption, that is, of the approach of the carbon disulphide molecules to the water molecules within the sphere of action of the molecules of alumina. In a similar manner, alumina prepared as described above causes the conversion of ethyl chloride into ethyl alcohol in the cold.

The hypothesis that adsorption always forms the basis of heterogeneous catalysis also furnishes a very simple explanation of those reactions in which the formation of intermediate chemical compounds is usually assumed, for instance, the reactions of Ipatiev, Sabatier, Bredig, etc. T. H. P.

A Laboratory Gas Meter. E. G. Beckett (*J. Soc. Chem. Ind.*, 1917, **36**, 52).—The apparatus consists essentially of a glass U-tube, the limbs of which are connected by a glass siphon, as shown in the annexed diagram. It is filled up to the dotted line *AB* with water (or other suitable mobile liquid), which thus fills the siphon, *C*. When the gas to be measured enters the apparatus, it forces the level of the water down in *A* and up in *B* until the difference in pressure causes the siphon to empty itself into *B*. The gas in *A* then escapes into *B* through the siphon, whilst the level of the water readjusts itself in the U-tube and the siphon again becomes filled. The process then starts again. The siphon runs over each time after a definite amount of gas has passed through the instrument, which amount, however, varies with the velocity of the gas.



The apparatus has the advantage that it can be used for corrosive gases, such as chlorine, for which the ordinary metallic gas-meter is quite unsuitable.

If a constant stream is desired, gas at a high pressure should be employed and the rate regulated or throttled immediately in front of the meter. H. W.

Inorganic Chemistry.

The Absolute Density of Hydrogen Bromide Gas. C. K. Reiman (*Compt. rend.*, 1917, **164**, 44—46).—Using the direct weighing method described by Moles (A., 1916, ii, 314, 526), determinations have been made of the weight of a normal litre of hydrogen bromide, the gas having been prepared either by the direct combination of hydrogen and bromine or by the action of syrupy phosphoric acid on potassium bromide, the resultant gas being purified in each case by fractional distillation of the liquefied gas. The value obtained, as a result of thirty-one determinations, for the weight of a normal litre of the gas is 3·6442 ± 0·0002 grams. W. G.

Electrolytic Oxidation of Sulphurous Acid. M. de K. Thompson and N. J. Thompson (*Met. and Chem. Eng.*, 1916, **15**, 677—679; from *J. Soc. Chem. Ind.*, 1917, **36**, 81).—The apparatus consisted of an earthenware cup as diaphragm containing a cylindrical nickel cathode with a cylindrical platinum gauze anode surrounding the diaphragm, the porous cup being filled either with sulphuric acid or sodium sulphite. The anodic compartment contained a solution of sulphur dioxide (1—5%); during electrolysis, the anode solution was kept saturated by passing in a current of sulphur dioxide. The current density was about 0·0075 ampere per sq. cm. Results proved that sulphurous acid is easily oxidised at platinum anodes to sulphuric acid of any concentration below 95%. The concentration of sulphuric acid in the cell has a great effect on the current efficiency, as also, but in a less degree, has the current density. Oxidation occurs with high current efficiencies even in concentrated sulphuric acid solutions. For a given concentration of sulphuric acid, the current efficiency decreases with increasing current density. H. W.

Catalytic Oxidation of Ammonia. E. Buch Andersen (*Zeitsch. Elektrochem.*, 1916, **22**, 441—443).—The oxidation of ammonia to nitric oxide and nitrogen dioxide has been investigated with regard to the connexion between the yield of oxide and the temperature and the rate of passage of the gas over the catalyst. It is shown that the yield of oxide is dependent on the temperature, but in the presence of the slightest excess of oxygen it is practically quantitative. Thus, varying the ammonia concentration from 2·5 to 5 volumes per cent., the temperature from 500° to 1000°, and the time of contact with the catalyst from 1·15 secs. to 0·18 sec., the author has been unable to detect any change in the amount of nitrogen dioxide produced. The amount of oxide produced depends mainly on the use of a catalyst which, whilst accelerating the oxidation, does not affect the decomposition of the oxide. It is stated that by use of a suitable catalyst it is possible at 500° to obtain a rapid and complete oxidation of ammonia, provided that the amount of ammonia does not exceed the amount corresponding with the oxygen admitted. J. F. S.

Preparation of Carbonyl Chloride. V. A. Plotnikov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 457—458).—The catalytic effect of salts is often explainable by the formation of complexes containing the catalyst and the substances reacting under its influence. Such complexes then undergo decomposition, which is induced either by temperature conditions or by the presence of compounds causing a diminution of the stability of the complexes. In this connexion interest attaches to the compounds of aluminium chloride with carbonyl chloride obtained by Baud (A., 1905, ii, 525).

[With Salatko-Petrischtsche.]—Carbonyl chloride is formed when carbon monoxide and chlorite are passed through a tube containing pieces of aluminium chloride at 30—35°, or, still better, if the gaseous mixture is passed through a saturated solution of aluminium chloride in chloroform; subsequent treatment of the chloroform solution with water yields a considerable quantity of carbon dioxide. T. H. P.

Borates: The System $Na_2O:B_2O_3:H_2O$ **at 60°. III.** U. Sborgi and F. Mecacci (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 455—458).—The complete diagram for this system at 60° is now given. The results show that the solubility of sodium oxide is 97·04 parts per 100 parts of water at 100°, this value being in accord with that usually accepted. Of the compounds formed at 60°, the 1 : 1 : 1 and the 2 : 1 : 1 ($Na_2O : B_2O_3 : H_2O$) compounds have not previously been described. T. H. P.

Preparation of Sodium Perborate. DEUTSCHE GOLD- & SILBER-SCHEIDEANSTALT VORM. ROESSLER (Brit. Pat., 100153, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 83).—A solution containing a carbonate (13—15% anhydrous) and an alkali borate is electrolysed, the borate reacting with the percarbonate formed to produce perborate. It is essential that the solution should be kept saturated with borax, and that solid perborate be always present; it is advisable that catalysts should be absent. This may be effected by using pure substances or by adding materials such as alkali hydrogen carbonate, stannic acid, or magnesium silicate (1—2 grams per litre of electrolyte). H. W.

Preparation of Alkali Perborates. DEUTSCHE GOLD- & SILBER-SCHEIDEANSTALT VORM. ROESSLER (Brit. Pat., 102359, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 83).—Sodium perborate is made by electrolysing lyes containing soda and borax. The accumulation of sodium hydrogen carbonate, produced during the action, must be restricted to a maximum of 70—75 grams per litre; otherwise the stability of the perborate is adversely affected. Hence, metaborate or free alkali and borax are added during the electrolysis; or lime, or other alkali, is added to the waste lye prior to its treatment or re-treatment. H. W.

The Double Salts of Cæsium Chloride with Calcium and Strontium Chlorides. GEORGE S. JAMIESON (*Amer. J. Sci.*, 1917, [iv], **43**, 67—68).—The double salt, $2CsCl,CaCl_2,2H_2O$, crystallises from solutions which contain very variable proportions of the two chlorides. The molar ratio may, in fact, be varied from $CsCl/CaCl_2 = 4$ to 0·25.

Solutions containing cæsium chloride and strontium chloride in the molar ratio 2 : 1 deposit crystals of the double salt,

$$5CsCl,2SrCl_2,8H_2O.$$

Cæsium chloride does not form a double salt with barium chloride. H. M. D.

Metallographic Study of the System Silver-Tellurium. MASUMI CHIKASHIGE and ISABURO SAITO (*Mem. Coll. Sci. Kyoto*, 1916, **1**, 361—368. Compare Pélabon, A., 1906, ii, 667; Pellini and Quercigh, A., 1910, ii, 1063).—Two compounds are formed, of which one, Ag_2Te, melts sharply at 957°, whilst the other, to which the formula Ag_7Te_4 is assigned, decomposes below its melting point, and exists in two modifications, each of which corresponds with a short branch of the freezing-point curve. β-Ag_7Te_4 is formed from Ag_2Te and liquid at 443°, and changes into the α-modification at 403°. Solid solutions are not formed. Eutectics occur at 32%

Ag and 350°, and at 87·5% Ag and 870° respectively. Annealing experiments indicate that the transformation is one of a single compound, and that a second compound, such as Ag_3Te_2, is not formed.

C. H. D.

Alloys of Certain Haloid Salts of Silver and of Alkali Metals. S. F. Shemtschushni (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 203—221. Compare A., 1907, ii, 258).—The systems NaBr–AgBr, NaCl–AgCl, and KBr–AgBr have been studied thermally and micrographically.

With NaBr–AgBr, results in accord with those of Sandonnini and Scarpa (A., 1914, ii, 204) have been obtained. The character of the cooling curves indicates the formation of an uninterrupted series of solid solutions, and the melting-point diagram corresponds with type I of Roozeboom's classification. The cooling curves, however, have not quite the simple form of those of solid solutions, but exhibit certain anomalies, depending on the generation of heat, almost at the completion of the solidification. The explanation of this phenomenon is as follows: Owing to the low velocity of diffusion, the crystals of the solid solution which separate first and are richer in sodium bromide do not absorb the amount of silver bromide required by the conditions of equilibrium at the given temperatures; in consequence of this, there remains an excess of almost pure silver bromide, which finally crystallises, and gives rise to a new halt on the cooling curve.

The melting-point results for the system NaCl–AgCl are almost identical with those obtained by Botta (A., 1911, ii, 293) and by Sandonnini (A., 1911, ii, 800), except that the melting points of sodium and silver chlorides are found to be 816° and 451° respectively. Both silver bromide and chloride exhibit changes of colour with change of temperature.

The results obtained with the system KBr–AgBr agree with those of Sandonnini (A., 1912, ii, 941), with the exception that the composition at the eutectic point, 285°, corresponds with 67 mol. % of silver bromide, and not with 56 mol. %.

Sections formed by the solidification of the mixtures between the microscope slide and cover-glass were examined in reflected light, both ordinary and polarised. The alloys of silver and sodium bromides exhibit structures similar to those of metallic solid solutions, the crystals being polyhedral and bordered by more or less thin lines, and, especially in the thicker sections, having a zonal structure resulting from the inadequate velocity of diffusion mentioned above. Similar appearances are observed with the system AgCl–NaCl. Sections containing more than 75 mol. % of sodium bromide or 60 mol. % of sodium chloride could not be prepared owing to the softening of the glass at the high temperatures required, but up to these limits the alloys are anisotropic. The structures of these sections and of those of the system AgBr–KBr are in complete correspondence with the melting-point diagrams.

T. H. P.

Lead Subiodide and an Improved Method for Preparing Lead Suboxide. The Solubility of Lead Iodide. HENRY GEORGE DENHAM (T., 1917, **111**, 29—41. Compare Denham and Allmand, T., 1908, **93**, 424).—In the earlier paper it has been shown that, in the presence of platinised platinum, hydrogen can reduce bivalent salts of lead to a lower state of valency. The treatment of lead suboxide with an acid or of a solution of a lead salt with metallic lead fails to produce lead sub-salts. However, by the action of methyl iodide vapour on a mixture of lead suboxide with four times its weight of silica at 260° in an atmosphere of nitrogen, it is possible to obtain lead subiodide, PbI (compare Denham, A., 1911, ii, 804), as a bright yellow solid, which on heating decomposes above 300°, with formation of lead iodide and metallic lead, a similar decomposition being effected by the action of acids. Lead subiodide appears to undergo slow oxidation in the air; it is much less soluble in water than is lead iodide, the solubility ratio, judged from the relative electrical conductivity of the two salts measured in a special apparatus, being approximately 1:9; the solution gives no trace of a precipitate with potassium chromate or hydrogen sulphide.

A determination of the solubility of ordinary lead iodide in water, based on the electrical conductivity of a saturated aqueous solution at 25° in a vacuum, and assuming complete dissociation, gave a result in exact agreement with that of von Ende (A., 1901, ii, 241; see also Lichty, A., 1903, ii, 480; Böttger, A., 1904, ii, 241).

The lead suboxide necessary for the above preparation of lead subiodide was obtained by the decomposition of lead oxalate at 270—335°, with continuous removal of the gaseous products by a mercury pump (compare Tanatar, A., 1901, ii, 451; Glaser, A., 1903, ii, 646; Brislee, T., 1908, **93**, 154). The product is a dark powder, which at 375° becomes paler in colour and somewhat less reactive towards methyl iodide, although its composition is unaltered.

For experimental details, see the original paper. D. F. T.

Reduction of Lead Sulphate. G. A. PERLEY and C. W. DAVIS (*J. Physical Chem.*, 1916, **20**, 151—163).—Whilst studying methods of regenerating sulphated accumulator plates, the authors noticed that when sodium hydroxide, lead, and lead sulphate were in contact simultaneously, crystals of lead were deposited. This reaction has been carefully studied in the present paper. It is shown that pure lead dissolves slowly in pure sodium hydroxide solution, but experiments under reduced pressure and in the absence of air failed to show any appreciable evolution of gas. The formation of lead crystals when lead, lead sulphate, and sodium hydroxide are in contact, is not dependent on impurities in the lead. All three substances are necessary, and the crystals are not obtained by the action of sodium hydroxide on lead or on lead sulphate. While the lead crystals are forming, the lead plate is being corroded, and the net result is a decrease in the total amount of metallic lead. The formation of lead crystals in alkaline solution is not due to fluctuations of temperature, with the intermediate formation and decomposition of a lead salt with a lower valency, although this is what happens in Denham's experiments with lead and lead acetate (T., 1908, **93**, 424). The rapid formation of fine lead crystals is due to a concentration cell consisting, in principle, of $Pb|NaOH|Na_2SO_4,PbSO_4|Pb$. The sodium hydroxide dissolves the lead sulphate, and the denser solution thus formed flows to the bottom of the container, while fresh sodium hydroxide flows in from above to replace it, thus setting up concentration differences. It is necessary to assume that the conversion of lead ions into plumbite ions takes time, and that the amount of lead sulphate dissolved as such is greater than it should be until equilibrium is reached. Rotating a sulphated lead strip makes the reduction more rapid and more uniform. This is not an argument against the reaction being due to a concentration cell. Rotating the electrode increases the removal of plumbite solution from the projecting portions of the electrode, but has less effect on the sunken portions, where there is more lead sulphate. We thus have the paradox that stirring increases the concentration differences, causing more rapid and more uniform reduction. On long keeping, large crystals of lead are formed at the lower edge of the sulphated plate. These continue to grow after all the lead sulphate has disappeared. These crystals are due to the action of a concentration cell consisting, in principle, of $Pb|\text{dil. } Na_2PbO_2|\text{conc. } Na_2PbO_2|Pb$. This can be duplicated by placing a lead strip in a test-tube, pouring in a concentrated solution of sodium hydroxide, and superposing a solution of lead sulphate in more dilute sodium hydroxide. Beautiful crystals of lead are then formed in the upper portion of the tube. J. F. S.

Iron Trisulphide and the Formation of Amorphous Iron Disulphide. V. RODT (*Zeitsch. angew. Chem.*, 1916, **29**, i, 422—423).—There being much uncertainty regarding the existence of iron trisulphide, the author has further investigated the subject, with the following results. When moist ferric hydroxide, or ferric hydroxide suspended in water, is treated with hydrogen sulphide, it becomes black, owing to the formation of ferric trisulphide, in accordance with the equation $2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 3H_2O$. In a moist condition in the absence of air, or in the presence of excess of hydrogen sulphide, it is transformed into a mixture of the disulphide and sulphide, thus: $Fe_2S_3 = FeS_2 + FeS$. This transformation takes about a week at the ordinary temperature, but only a few hours at 60°. The mixture thus produced is only partly soluble in dilute hydrochloric acid, whereas the trisulphide is readily and completely soluble. The transformation is prevented, in the absence of air, by small quantities of alkali, and even magnesium carbonate and calcium carbonate have a retarding effect. When dried in a vacuum over phosphoric oxide, iron trisulphide is very stable.

When exposed to the action of the air in the presence of alkaline substances, ferric trisulphide gradually becomes light yellow in colour, sulphur being deposited. The product resembles limonite in appearance, and when dried gives a fine, yellow powder containing a constant percentage of water, which is less than that corresponding with ferric hydroxide.

The above results are used to explain the various discrepancies found in the literature with respect to ferric trisulphide.

Feld's statement that iron disulphide is formed when precipitated ferrous sulphide is boiled with flowers of sulphur is confirmed; even ordinary ferrous sulphide, if finely powdered, and finely powdered crystalline sulphur, act in the same way. Iron disulphide is also formed when a solution of sodium trisulphide is added slowly to a boiling solution of ferrous sulphate, sulphur being liberated at the same time. Care must be taken that at no time is the sodium trisulphide in excess, otherwise the formation of iron disulphide is prevented.

Bischof's observations on the production of iron pyrites in nature ("Lehrb. chem. physik. Geologie," I, 357, 917) are in complete agreement with the fact that the final product of the action of hydrogen sulphide on ferric hydroxide in the absence of alkaline substances is iron disulphide. T. S. P.

Metallographic Study of the System Antimony Sulphide–Cuprous Sulphide. MASUMI CHIKASHIGE and YOSHINDO YAMAUCHI (*Mém. Coll. Sci. Kyoto*, 1916, 1, 341—347. Compare Pélabon, A., 1905, ii, 435; Parravano and de Cesaris, A., 1912, ii, 942).—The sulphides are fused together in Jena-glass or porcelain tubes in nitrogen. The freezing-point curve has two maxima, corresponding with $4Cu_2S,5Sb_2S_3$, melting at about 520°, and $3Cu_2S,Sb_2S_3$, melting at 571°. There are eutectic points at 7%, 37%, and 68% of cuprous sulphide, the eutectic temperatures being 463°, 514°, and 562° respectively. Solid solutions are not formed. The microscopical examination confirms the thermal results. It has not been determined whether the native mineral chalcostibite, usually regarded as the metathioantimonite, has the formula Cu_2S,Sb_2S_3 or $4Cu_2S,5Sb_2S_3$. The second compound described above may be regarded as cuprous orthothioantimonite. C. H. D.

The Probable Movement of Atoms in Bismuth during Crystal Gliding. A. JOHNSEN (*Centr. Min.*, 1916, 385—392).—The existence of two sets of gliding-planes in rhombohedral crystals of bismuth, considered in connexion with the structure of the point-system and *X*-ray analysis, indicates that the molecules are diatomic and that these possess the same degree of symmetry as the whole crystal. The atomic centres are $3{\cdot}10^{-8}$ cm. apart. This agrees with the facts that bismuth dissolved in a large quantity of lead is diatomic, and that the vapour density of bismuth at 1600—1700° lies between that for Bi and Bi_2. L. J. S.

The Melting Point of Palladium and Wien's Constant C_2. G. HOLST and E. OOSTERHUIS (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 549—550).—The constant c_2 in Wien's radiation formula, $\lambda \log E_1/E_2 = c_2(1/T_2 - 1/T_1)$, in which E_1 and E_2 are the emissive powers of the black body at the melting points of palladium (T_1) and gold (T_2) respectively, is for $\lambda = 0{\cdot}6563\,\mu$ equal to 14465 ± 5 if the melting point of palladium is taken as 1549°. If in accordance with the scale of the Physikalische Technische Reichsanstalt $c_2 = 14300$, the formula gives 1557° as the melting point.
H. M. D.

Mineralogical Chemistry.

Occurrence of Silver in Argentiferous Galena Ores. ARVID E. NISSEN and SAMUEL L. HOYT (*Economic Geology*, 1915, **10**, 172—179).—In order to determine the state in which silver exists in argentiferous galena, fusions of lead and silver sulphides were examined. The following conclusions are drawn: (1) Silver occurs as argentite in some primary and in some secondary argentiferous galena ores. (2) The limit of solid solution at atmospheric temperatures is below 0·2% Ag_2S. (3) The eutectic, as given by Friedrich (1907), is not developed in concentrations below 2·70% Ag_2S.
L. J. S.

Minium from Biberwier, Tyrol. E. DITTLER (*Centr. Min.*, 1916, 521).—This occurs as an alteration product of galena, the red nodules still containing a nucleus of galena. Analysis (Pb, 80·60; S, 6·33; gangue, 8·29 = 95·22%) proves the presence of galena 47·17, with minium (Pb_3O_4) 43·81%. The alteration has been effected by weathering, probably with a basic carbonate as an intermediate stage.
L. J. S.

The Refractive Indices of Rhombohedral Carbonates. PAUL GAUBERT (*Compt. rend.*, 1917, **164**, 46—49).—Determinations of the refractive indices have been made on a number of mineral carbonates, the values obtained being as follows: for giobertite, $\epsilon = 1{\cdot}5148$—$1{\cdot}5170$, $\omega = 1{\cdot}7053$—$1{\cdot}7115$; for siderite, $\epsilon = 1{\cdot}5982$—$1{\cdot}6020$, $\omega = 1{\cdot}7959$—$1{\cdot}8120$; for dialogite, $\epsilon = 1{\cdot}5934$—$1{\cdot}6053$, $\omega = 1{\cdot}8100$—$1{\cdot}8194$; for a cupriferous smithsonite, $\epsilon = 1{\cdot}612$, $\omega = 1{\cdot}782$; for dolomite, $\epsilon = 1{\cdot}5021$—$1{\cdot}5133$, $\omega = 1{\cdot}6808$—$1{\cdot}6946$; for ankerite, $\epsilon = 1{\cdot}5148$—$1{\cdot}5273$, $\omega = 1{\cdot}7046$—$1{\cdot}7172$; for mesitite, $\epsilon = 1{\cdot}5873$, $\omega = 1{\cdot}7632$. The values calculated from the chemical composition, using the laws governing the relations between the indices of an isomorphous mixture, agree often only approximately with those found, this being due to the fact that specimens from the same locality often show slight variations in composition. The author has found that the refractive indices may vary even in the same crystal, owing to zone structure in the crystal.
W. G.

Dahllite from Kangerdluarsuk, Greenland. O. B. Bøggild (*Jahrb. Min.*, 1916, ii, Ref. 163—165; from *Meddelelser om Grönland*, 1915, **51**, 434—443).—The rock naujaite occurring at Kangerdluarsuk and other localities in the neighbourhood of the Tunugdliarfik-Fjord, in south Greenland, contains in crevices crusts of natrolite and dahllite. The latter forms small, hexagonal plates ($n = 1·623—1·627$, $\omega - \epsilon = 0·011$), agate-like, banded masses ($\epsilon = 1·591—1·607$, $\omega = 1·604—1·626$, $\omega - \epsilon = 0·012—0·017$; D 3·000—3·012 and 3·090—3·094), and layers of amorphous material ($n = 1·605—1·619$). These optical determinations, although varying widely, differ from the constants for apatite. Analysis by C. Christensen of the agate-like variety gave the following results, with the ratio $CaO : P_2O_5 = 4 : 1$, thus differing from the apatite ratio and also somewhat, from the Norwegian dahllite.

P_2O_5.	CaO.	Al_2O_3.	Na_2O.	CO_2.	H_2O.	Total.
32·40	54·10	3·15*	0·77	8·26	1·32	100·00

* Including: FeO, 0·79; K_2O, 0·11.

A study of the optical constants and specific gravity as functions of the chemical composition of the phosphorite minerals leads to no definite result, but these minerals are to be regarded as distinct from apatite. L. J. S.

New Phosphates from Greifenstein, Saxony. F. Slavík (*Jahrb. Min.*, 1916, ii, Ref. 31—34; *Abh. böhm. Akad.*, 1914, No. 4, 19 pp.).—*Ježekite*, at first erroneously referred to as "epistilbite," forms colourless to white monoclinic prisms, needles, and plates, $a : b : c = 0·8959 : 1 : 1·0241$; $\beta = 105°31\frac{1}{2}'$. Cleavage (100) perfect. $H = 4\frac{1}{2}$; $D = 2·940$; refractive indices, $\alpha = 1·55$, $\beta = 1·56$, $\gamma = 1·59$. Analysis I, by E. Skarnitzl, gives the formula $P_2O_5,Al_2O_3,CaO,2NaF,2NaOH$ or $(PO_4)_2F_2(OH)_2Al(AlO)CaNa_4$.

Roscherite, a new mineral of the childrenite group, forms dark brown columns or plates. Monoclinic, $a : b : c = 0·94 : 1 : 0·88$; $\beta = 99°50'$; cleavage (001) and (010) good. $H = 4\frac{1}{2}$; $D = 2·916$; $n = 1·625—1·63$. Analysis II, by K. Preis, gives the formula $(Mn,Fe,Ca)_2Al(OH)P_2O_8,2H_2O$.

Lacroixite, at first mistaken for "herderite," is pale yellow or green and indistinctly crystallised; probably monoclinic and pseudo-rhombic ($a : b : c = 0·82 : 1 : 1·60$). $H = 4\frac{1}{2}$; D 3·126; $n = 1·57$. Analysis III, by A. Jilek, gives $Na_4(Ca,Mn)_4Al_3P_3O_{16}(F,OH)_4,2H_2O$, or nearly $2NaR''(AlO)PO_4F,H_2O$.

	P_2O_5.	Al_2O_3.	FeO.	MnO.	CaO.	Na.	Li.	F.	H_2O.	Total.
I.	30·30	21·92	—	trace	13·50	18·71	0·86	8·15	—	100·70*
II.	35·98	13·01	9·58	13·70	10·87	trace	—	—	11·52	99·24†
III.	28·92	18·92	—	8·45	19·51	—	—	—	4·22	100·00‡

* Including: OH, 7·26; Fe_2O_3, trace. † Including: insoluble residue 4·58%.
‡ Including: NaF, 14·47; NaOH, 5·51%.

L. J. S.

Crandallite, a New Mineral. G. F. LOUGHLIN and W. T. SCHALLER (*Amer. J. Sci.*, 1917, [iv], **43**, 69—74).—This new hydrated phosphate of calcium and aluminium is found as compact to cleavable masses filling irregularly shaped cavities in a quartz-barytes gangue with pyrites, enargite, etc., in the Brooklyn mine, Silver City, Tintic District, Utah. It is white to grey with shades of yellow or brown. Under the microscope the cleavage plates are seen to be composed of fine radiating fibres, and it is probable that the cleavages represent a pre-existing mineral (goyazite ?), the alteration of which has given rise to the fibrous crandallite. In addition to this, the material is much confused by the presence of large amounts of impurities in fine dissemination. The mineral is soluble in acids. Analysis by W. T. SCHALLER gave, after deducting 35·13% soluble:

Al_2O_3.	CaO.	SrO.	MgO.	P_2O_5.	SO_3.	H_2O at 105°.	H_2O > 105°.	Total.
38·71	7·50	2·21	0·94	27·09	3·80	1·29	18·86	100·40

This gives the formula $CaO,2Al_2O_3,P_2O_5,5H_2O$, with slight replacement of CaO by SrO and MgO, and of P_2O_5 by SO_3, or, more exactly, of $(HPO_4)''$ by $(SO_4)''$, conforming with the type of the gorceixite formula ($BaO,2Al_2O_3,P_2O_5,5H_2O$), and differing slightly from that of goyazite ($2SrO,3Al_2O_3,2P_2O_5,7H_2O$). It is suggested that crandallite and gorceixite belong to a group of fibrous minerals which have been produced by the alteration of minerals of the closely allied alunite–beudantite group. L. J. S.

Natrojarosite from Kundip, Western Australia. EDWARD S. SIMPSON and MAURICE A. BROWN (*J. Roy. Soc. Western Australia*, 1916, **1** (for 1914–1915), 45—54).—Dull, porous, ochre-yellow masses of natrojarosite occur in oxidised gold ore on the Harbour View mineral lease at Kundip in the Phillips River gold-field. Under the microscope, the material is seen to be minutely crystalline in rhombohedral scales. Analysis agrees closely with the formula $Na_2O,3Fe_2O_3,4SO_3,6H_2O$ or $Na_2[Fe(OH)_2]_6(SO_4)_4$. The material is only slowly attacked by hot concentrated nitric acid, but is dissolved by hot concentrated hydrochloric acid, and it is readily decomposed by a hot solution of sodium hydroxide. There is no loss at 150°; at a red heat all the water and three-quarters of the sulphuric anhydride are expelled. The mineral has probably been formed by the weathering of pyritous ore in the presence of sodium-bearing rocks and ground waters.

Na_2O.	K_2O.	Fe_2O_3.	FeO.	SO_3.	P_2O_5.	H_2O.	Total.	Sp. gr.
6·32	0·68	49·86	0·16	32·30	0·20	10·93	100·45	3·11

L. J. S.

Composition of Thaumasite from Great Notch, New Jersey. GLENN V. BROWN (*Amer. Mineralogist*, 1916, **1**, 81).—Analysis of material from a 100-lb. mass of thaumasite, found about 1908 in the basalt of the Francisco quarry at Great Notch, gave the following results, agreeing closely with the formula $CaCO_3,CaSiO_3,CaSO_4,15H_2O$.

CaO.	MgO.	$(Al,Fe)_2O_3$.	CO_2.	SiO_2.	SO_3.	H_2O (below 100°).	H_2O (above 100°).	Total.
27·18	0·02	0·20	7·97	9·36	13·03	0·32	42·24	100·31

L. J. S.

The System Anorthite-Forsterite-Silica. H. E. BOEKE (*Centr. Min.*, 1916, 313—317).—A criticism and discussion of Andersen's paper (A., 1915, ii, 361). The quaternary system $CaO-MgO-Al_2O_3-SiO_2$ may be represented by means of a regular tetrahedron with these components placed at the four corners. Besides the compounds forsterite ($2MgO,SiO_2$), clinoenstatite (MgO,SiO_2), diopside ($MgO,CaO,2SiO_2$), anorthite ($CaO,Al_2O_3,2SiO_2$), and spinel (MgO,Al_2O_3), there is a possibility of others, namely, calcium silicates ($CaSiO_3$, $Ca_3Si_2O_7$, Ca_2SiO_4, Ca_3SiO_5), gehlenite ($2CaO,Al_2O_3,SiO_2$), sillimanite (Al_2O_3,SiO_2), cordierite ($2MgO,2Al_2O_3,5SiO_2$), and garnet ($3[Ca,Mg]O,Al_2O_3,3SiO_2$). L. J. S.

Natural and Artificial Ultramarine. C. DOELTER (*Jahrb. Min.*, 1916, ii, Ref. 24; from *Sitzungsber. Akad. Wiss. Wien, Math.-naturw. Kl.*, Abt. I, 1915, **124**, 37—48).—As opposed to Brögger and Bäckström (1890), who regarded ultramarine, lazulite, haüyne, and sodalite as atomic compounds, these are considered to be molecular compounds of the nephelite silicate, $NaAlSiO_4$, with $NaCl$, Na_2SO_4, Na_2S, NaS, NaS_2, etc. The coloration of ultramarine appears to depend on the presence of free colloidal sulphur or polysulphides; in white ultramarine these are not present, only Na_2S. Support to this view is given by the action of radium emanations on ultramarine of various colours. L. J. S.

Leifite, a New Mineral from Narsarsuk, Greenland. O. B. BÖGGILD (*Jahrb. Min.*, 1916, ii, Ref. 161—162; from *Meddelelser om Grönland*, 1915, **51**, 427—433).—The new mineral occurs with felspar, aegirite, and zinnwaldite in the drusy pegmatite veins at Narsarsuk, near Julianehaab. It is colourless to white, with a faint violet sheen, and has the form of hexagonal prisms, without terminal faces, reaching to 2 cm. in length and 5 mm. in thickness. There is a perfect cleavage parallel to the prism faces and a conchoidal cross-fracture. $H=6$, $D=2\cdot565-2\cdot578$. Optically uniaxial and positive, $\epsilon=1\cdot5224$, $\omega=1\cdot5177$. The mineral is not decomposed by hydrochloric acid. It fuses extremely easily, with intumescence, to a colourless glass. Analysis by C. CHRISTENSEN gave:

SiO_2.	Al_2O_3.	MnO.	Na_2O.	F.	H_2O.	Total (less O for F).
67·55	12·69	0·41	15·47	4·93	0·77	99·74

This gives the formula $Na_2Al_2Si_9O_{22},2NaF$ or $Na_4(AlF)_2Si_9O_{22}$.

The degree of acidity is greater than in the acid silicates, petalite, and milarite, and is exceeded only in the Greenland minerals neptunite, narsarsukite, and lorenzenite. L. J. S.

An American Occurrence of Miloschite. EDGAR T. WHERRY and GLENN V. BROWN (*Amer. Mineralogist*, 1916, **1**, 63—67).—A blue, earthy mineral found in a gossany vein near Ely, Nevada, resembling chrysocolla in appearance, but containing no copper, is identified with the Serbian miloschite. The optical characters of the minute, crystalline grains suggest monoclinic symmetry; refractive indices, $\alpha=\beta=1{\cdot}552$, $\gamma=1{\cdot}559$. The following mean of two analyses by G. V. BROWN gives the kaolinite ratios $H_4R'''_2Si_2O_9$. The mineral may thus be regarded as a chromiferous kaolinite, corresponding with fuchsite, the chromiferous variety of muscovite, from which it has no doubt been derived.

SiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	H_2O at 105°.	H_2O at 300°.	Total.
43·47	34·41	3·85	0·86	0·37	0·12	0·28	3·54	13·27	100·17

L. J. S.

Mineralogical Notes. ESPER S. LARSEN and GEORGE STEIGER (*J. Washington Acad. Sci.*, 1917, **7**, 6—12).—Aphrosiderite from British Columbia.—A fossiliferous slate of Cambrian age occurring near Field, in British Columbia, carries numerous veinlets of pale green chlorite with some pyrites and calcite, the veinlets being roughly parallel to one another and perpendicular to the cleavage of the slate. The slate is very fine in texture, and is made up largely of muscovite, with some kaolinite and very little quartz, apatite, and pyrites: analysis I. The chlorite has H 1—2, D 2·959, *n* 1·625, and is almost isotropic; anal. II is near

$$5(Fe,Mg)O,2Al_2O_3,4SiO_2,5H_2O,$$

which lies between the formulæ usually assigned to aphrosiderite and delessite.

Thuringite from Colorado.—This occurs in large amount as a primary filling in the metalliferous veins cutting rhyolite near Creede. It is green, soft and friable, and fibrous to platy in structure. Material from different mines shows variations in the refractive indices (*n* 1·585—1·643), suggesting variations in chemical composition. Anal. III of material from the Last Chance mine on the Amethyst vein.

Griffithite, a new member of the chlorite group.—This occurs as a filling in amygdaloidal cavities in basalt at Cahuenga Pass, Griffith Park, Los Angeles, California. It differs both optically and chemically from any chlorite previously described. It is dark green, H about 1, D 2·309; fusible at 4, with intumescence to a black, magnetic slag; and gelatinised by hydrochloric acid. It is optically negative, with the first mean line normal to the perfect basal cleavage, $2V=0°—40°$, $\alpha=1{\cdot}485$, $\beta=1{\cdot}569$, $\gamma=1{\cdot}572$; pleochroism, pale yellow to brownish-green. Analysis IV gives the formula $4(Mg,Fe,Ca)O,(Al,Fe)_2O_3,5SiO_2,7H_2O$.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.
I.	54·49	25·60	0·89	2·00	1·18	1·90	0·28	6·67
II.	24·97	23·76	1·55	26·86	10·81	trace	0·26	0·97
III.	24·34	16·46	12·04	28·89	5·41	nil	0·37	trace
IV.	39·64	9·05	7·32	7·83	15·80	2·93	0·71	nil

	H_2O at 105°.	H_2O >105°.	TiO_2.	Total.
I.	0·33	3·91	0·72	99·83*
II.	10·71		0·11	100·00
III.	0·35	9·19	trace	99·80†
IV.	12·31	4·90	nil	100·49

*Including: CO_2, 1·54; P_2O_5, 0·08; S, 0·24; CuO, trace. †Including: MnO, 2·75; CO_2, P_2O_5, S, traces.

L. J. S.

Minerals from the Manganese Ore Deposits of Oberhalbstein, Grisons, Switzerland. F. P. Müller (*Centr. Min.*, 1916, 457—459).—Small, lenticular masses of oxidised manganese ore occur in schistose rocks associated with serpentine at this locality. The minerals present include zoisite, epidote, piedmontite, rhodochrosite, rhodonite, and a hydrous manganese silicate. The last is reddish-brown, with a metallic lustre. H=3½, D slightly less than that of quartz (2·65), *n* 1·54—1·55, birefringence 0·025—0·027; optically negative and usually uniaxial. Analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	CuO.	Na_2O.	K_2O.	H_2O.	Total.
47·15	5·09	0·36	36·89	trace	2·99	trace	0·07	1·21	6·24	100·00

L. J. S.

Titaniferous Augite from Ice River, British Columbia. Charles H. Warren and John A. Allan, with analysis by M. F. Conner (*Amer. J. Sci.*, 1917, [iv], **43**, 75—78).—A black, strongly pleochroic augite is present in the basic (melanocratic) separations from the nephelite-syenite magma of this district, forming at times the greater part of the rock, which then becomes an augitite. It has the form of small grains or prisms, and is remarkable in containing numerous rod-like inclusions arranged parallel to the *a*- and *c*-axes of the crystal. These inclusions are black and opaque, and are probably ilmenite. The extinction-angle of the augite on the plane of symmetry is 42·3°. Analysis shows the presence of much titanium dioxide, exceeding any previously recorded (TiO_2 2·85% in augite from a monchiquite from Rio de Janeiro). It is suggested that the ilmenite molecule, $RTiO_3$, may have crystallised out isomorphously with the metasilicate molecule, $RSiO_3$, of the augite, and that, subsequently becoming unstable in that state, it separated out, and is now represented by the inclusions of ilmenite.

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	MnO.	H_2O.	Total.	Sp. gr.
41·80	4·84	9·30	5·44	3·30	10·82	22·89	0·10	1·26	99·75	3·39

L. J. S.

Iron Meteorite from Cookeville, Tennessee. GEORGE P. MERRILL (*Proc. U.S. Nat. Museum*, 1916, **51**, 325—326).—A much weathered mass, weighing 2132 grams, was found about three years ago at Cookeville, Putnam County. It shows a very regular and coarse octahedral structure with bands 2—6 mm. wide of kamacite and very thin plates of taenite. Analysis by J. E. WHITFIELD gave:

Fe.	Ni.	Co.	Fe_2O_3.	NiO.	P.	C.	S.	SO_3.	Ignition.	Total.
61·33	6·38	0·37	27·89	1·10	0·17	0·20	0·38	0·09	2·75	100·66

L. J. S.

The Meteoric Irons of Whitfield Co., Georgia. GEORGE P. MERRILL (*Proc. U.S. Nat. Museum*, 1916, **51**, 447—449).—The following new analysis, by J. E. WHITFIELD, is given of the 117-lb. mass found near Dalton, Whitfield Co., which was first described and analysed by C. U. Shephard (A., 1884, 30).

Fe.	Ni.	Co.	Fe_2O_3.	Cu.	Pt.	Ir.	Si.	S.	P.	C.	Total.
91·469	7·575	0·550	0·350	0·016	trace	0·002	0·001	0·025	0·095	0·004	100·087

Although similar in chemical composition to the Whitfield Co. iron described by W. E. Hidden (A., 1882, 153), it differs essentially in structure, as shown on the etched surfaces, and the two irons belong to distinct falls. The Cleveland, Tennessee, iron described by G. F. Kunz in 1887 is also distinct. L. J. S.

Analytical Chemistry.

Estimation of Free and Combined Sulphur in Vulcanised Rubber, and the Rate of Combination of Sulphur with Different Types of Plantation Para Rubber. B. J. EATON and F. W. F. DAY (*J. Soc. Chem. Ind.*, 1917, **36**, 16—20).—The sample is finely divided and extracted for one hundred hours with boiling acetone in a Beadle and Stevens apparatus (A., 1913, ii, 444). The paper packet containing the extracted substance (the weight of the sample taken should be 0·1374 gram) is placed in a small glass tube closed at one end; this is inserted in a combustion tube and the paper and its contents are burnt in a current of oxygen. The gases evolved are collected in receivers containing small quantities of 7*N*-sodium hydroxide solution. When the combustion is completed, the contents of the receivers are treated with hydrochloric acid containing bromine, and the resulting sulphuric acid is precipitated as barium sulphate. The "free" sulphur in the acetone solution is estimated by evaporating the solvent and oxidising the residue first by evaporation with nitric acid and bromine and then by fusion with a mixture of sodium and potassium carbonates, potassium nitrate, and potassium chlorate. After the fused mass has been dissolved in dilute hydrochloric acid, the sulphuric acid is precipitated as barium sulphate. Experiments made with different types of Para rubber showed that the rates at which they combined with sulphur were in accordance with their different rates of cure as determined by their physical properties in the load–stretch curves; the percentage of combined sulphur at the optimum time of cure was practically the same (4—4·5%) for all three types. W. P. S.

Estimation of Small Quantities of Arsenic. PETER KLASON (*Arkiv Kem. Min. Geol.*, 1916, **6**, No. 5, 1—16).—The author has investigated fully the Fresenius–von Babo method for the estimation of small quantities of arsenic. In order to obtain known quantities of arsenic, standard solutions of arsenious and arsenic acid were prepared, and aliquot portions of these evaporated to dryness for the purposes of the estimation. When arsenious sulphide was used, it was prepared from a known volume of the above standard solutions by precipitation with thioacetic acid, followed by evaporation to dryness; the residue was then dissolved in a dilute solution (2%) of sodium carbonate, and the solution again evaporated to dryness. For the estimation, the dry residues were mixed with a mixture of 3 parts of sodium carbonate to 1 part of potassium cyanide, and the mixture transferred to a bulb tube, the bulb having a volume of about 3·5 c.c. The bulb was heated by a ring burner, supplied with a 20 cm. high draught-chimney, whilst a stream of carbon dioxide was passed through it. In order to prevent the arsenic subliming back, a piece of thick glass rod was put in the tube behind the bulb; the tube where the arsenic condensed was a capillary In the first experiments, in accordance with the instructions usually given, the carbon dioxide was dried before passing through the tube, but it was found that this was not necessary. In later experiments the gas was simply washed and then passed through a tube containing cotton-wool, before coming to the bulb tube. The capillary tube must be quite clean and free from all traces of grease. When the deposition of arsenic was complete, the capillary tube was cut off and weighed on a micro-balance; it was then heated in an argand burner to expel the arsenic, and again weighed when cool, in order to determine the weight of arsenic.

The results obtained, taking weights of arsenic oxide or sulphide varying between 0·0375 and 1·125 mg., were very variable and far from quantitative, the estimated quantities varying from 42% to 95% of the quantities actually taken. The loss was shown not to be due to arsenic remaining behind as sodium arsenide in the reduction mixture, but to be caused by some of the arsenic vapour being carried away in the stream of carbon dioxide. This was proved by attaching to the capillary of the bulb tube another (straight) tube packed with small bits of porcelain followed with a layer (3 mm.) of asbestos, this tube also ending in a capillary. During the estimation the asbestos layer became more or less dark, owing to the deposition of arsenic. When this arsenic was driven over into the capillary tube (in a stream of pure hydrogen) and its quantity estimated on the microbalance, the amount found accounted for the low percentages mentioned above. By this means quantitative results could be obtained.

A number of estimations of arsenic by the sodium carbonate–potassium cyanide method, as usually carried out (in Sweden), showed the accuracy to be about 90%.

The reaction which takes place when the above reaction mixture is used cannot be simply the formation of potassium cyanate with the liberation of arsenic, since sodium carbonate is present. Reasons are given in support of the scheme: $5NaAsO_2 = 3NaAsO_3 + As_2 + Na_2O$. The sodium arsenate is then reduced by the potassium cyanide to arsenite, which again gives arsenate and arsenic, and so on to completion. It is further shown that if arsenic is present as a salt of ortho-arsenious or -arsenic acid, as is the case when magnesia is added to the reaction mixture, no reduction takes place. When the arsenic is present as sulphide, reaction takes place according to the equation: $As_2S_3 + 3Na_2CO_3 = As_2O_3 + 3Na_2S + 3CO_2$; reduction then takes place as above, no thiocyanate being formed.

The above method cannot be used when organic matter is present, but can be replaced by the following modification of Berzelius's method. The residues containing arsenic, if the latter is present as sulphide, are evaporated down to dryness with concentrated nitric acid. The residue is then mixed with a mixture of equal parts of sodium carbonate and potassium carbonate and a little mercuric oxide, and the resulting mass put into the bulb tube and heated in a stream of oxygen until it is quite white and mercury is no longer deposited in the capillary. It is then reduced in a stream of hydrogen which has been purified by passing through dilute solutions of silver nitrate and mercuric chloride. The arsenic deposited in the capillary is then weighed as given above. The temperature to which the bulb is heated should be such that the reaction mixture does not fuse. If fusion takes place and magnesia is present, ortho-salts are formed, and these are no longer reduced by hydrogen, as mentioned above. Using quantities of arsenious oxide containing from 0·19 to 0·38 mg. of arsenic, good quantitative results were obtained. T. S. P.

Estimation of Boric Acid by Titration in the Presence of Glycerol. B. H. St. John (*Amer. J. Pharm.*, **89**, 8—10).—Methyl-red is a better indicator than is methyl-orange in the neutralisation of borate solutions previous to the titration of the boric acid in the presence of glycerol and phenolphthalein.

W. P. S.

[Sources of Error in the Analysis of Volatile Substances which are difficult to Burn, and a Method by which Accurate Results can be obtained]. C. J. Enklaar (*Rec trav. chim.*, 1917, **36**, 244—246).—See this vol., i, 112.

Determination of the Free Alkali Hydroxide in Soap. V. A. Izmailski (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 411—432). —For the determination of the free alkali hydroxide in soap neither the alcohol method nor the barium chloride method gives results which are accurate or reproducible by different workers. The errors of the alcohol method are due principally to: (1) the capability of colloidal soap in an alcoholic medium to adsorb free alkali, and (2) the sparing solubility in alcohol of the "alkali soap" thus formed and its marked retention of the filtrate. When barium chloride is used, special precautions are necessary to prevent hydrolysis of the soap itself. From the results of experiments made by the author, the following method has been derived.

Of the soap, freshly cut from the middle, *a* grams (about 10) are weighed into a flask of about 400 c.c. capacity fitted with a rubber stopper, and dissolved in 20*a* c.c. of boiling distilled water. To the hot solution are gradually added 2*a* c.c. of neutralised (towards phenolphthalein) barium chloride solution containing 30 grams of the salt to 100 grams of water, the liquid being rotated and boiled for a short time as long as the precipitate does not settle. During the dissolution and boiling, the flask is loosely closed with the stopper. When the precipitate settles, the flask is cooled under the tap and tightly stoppered, the cold liquid being immediately filtered through a rapid filter into a conical flask and the filter washed with cold boiled water. Any precipitate remaining in the original flask is washed with three portions of boiled and cooled water, amounting in all to 10*a* c.c., in the closed flask. The liquid is titrated with decinormal acid in presence of phenolphthalein.

The values thus obtained, which the author terms the "alkali numbers," are characteristic for different types of soap. T. H. P.

Volumetric Estimation of Zinc in Zinc Chloride, Nitrate, and Sulphate. F. W. Sjöstrom (*Farm. Revy.*, 1916, 489—491; *Zeitsch. angew. Chem.*, 1916, **29**, Ref. 511; from *J. Soc. Chem. Ind.*, 1917, **36**, 82).—If an alkaline solution of zinc chloride, nitrate, or sulphate, of known alkali content, is treated with excess of pure hydrogen peroxide solution, the zinc is precipitated quantitatively as zinc perhydroxide and a certain quantity of alkali is neutralised by the liberated anion. The excess of alkali is titrated and the quantity of zinc calculated, allowance being made for any free acid present in the original zinc solution before being made alkaline. H. W.

Estimation of Nickel in Iron Ores. P. Covitz (*Met. and Chem. Eng.*, 1916, **15**, 682—683; from *J. Soc. Chem. Ind.*, 1917, **36**, 87).—The following method, using dimethylglyoxime, is accurate and reasonably rapid; it does not require the removal of other elements. One gram of the finely powdered ore (100—120 mesh) is dissolved in nitric acid (*D* 1·42, 10 c.c.) and hydrochloric acid (*D* 1·2, 10 c.c.), these quantities being varied to suit the nature of the ore; sufficient nitric acid must be used to oxidise all reduced metals, particularly ferrous iron. After cooling, sulphuric acid

(*D* 1·84, 10 c.c.) is added, and the solution is evaporated until copious white fumes appear. Nitric acid must be expelled completely, or it will interfere in the later stages. The solution is cooled, treated first with water (30 c.c.), then with hydrochloric acid (2—3 c.c.), heated for ten to fifteen minutes, after which tartaric or citric acid (5 grams) is added. The solution is filtered, the filtrate diluted to 125 c.c., and neutralised with ammonia. If on passing the neutral point the solution is brown, enough citric acid is added to produce a green colour. After the solution has been faintly acidified with hydrochloric acid and heated to 70—85°, the nickel is precipitated by the addition of dimethylglyoxime reagent (20 c.c.; 8 grams of dimethylglyoxime in 1 litre of ethyl alcohol); the solution is stirred constantly and allowed to boil. The precipitate is collected in a weighed Gooch crucible and dried at 110° for forty-five minutes. The dried precipitate contains 20·31% of nickel. H. W.

New Method of Precipitation of Platinum Sulphide, and Analysis of Platinised Asbestos. V. N. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 527—529).—The addition of mercuric chloride to a platinum solution prior to precipitation of the metal as sulphide facilitates the estimation of platinum and allows of accurate results being obtained (compare Gaze, A., 1913, ii, 440), but the bulk of the precipitate is greatly increased and injurious mercury vapour is liberated when the precipitate is ignited.

The incomplete precipitation of platinum sulphide under ordinary conditions depends on the formation of a stable colloidal solution of the sulphide, and the author finds that the hydrosol is converted into the insoluble hydrogel if magnesium chloride is present in the solution. The method employed is as follows.

A weighed quantity of about 5 grams of platinum chloride is dissolved in water in a 250 c.c. flask, the solution being made up to volume and mixed. Twenty-five c.c. of this liquid are diluted to about 200 c.c. in a 250—300 c.c. beaker and then treated with a few drops of hydrochloric acid and about 5 grams of magnesium chloride, either in solution or as crystals, per 100 c.c. of liquid. A rapid current of hydrogen sulphide is then passed through the solution until the latter is saturated, the precipitate adherent to the gas-delivery tube being removed by a piece of filter-paper, and the latter dropped into the liquid, which is then boiled until all odour of hydrogen sulphide has disappeared. The platinum sulphide is washed twice by decantation and several times on the filter with water acidified with one or two drops of hydrochloric acid, the wet filter being then charred in a covered platinum crucible and finally ignited in a blow-pipe flame. This method gives results in very close agreement with those obtained electrolytically.

In the case of platinised asbestos, this is treated on a water-bath with aqua regia, which dissolves the platinum and also sufficient magnesium salts to render the subsequent addition of magnesium chloride superfluous. Ten grams of the asbestos are heated in a large beaker with excess of aqua regia (2 parts of hydrochloric and

1 part of nitric acid) on a water-bath until all the black particles disappear from the asbestos and the liquid assumes an orange-yellow colour. The contents of the beaker are carefully poured into a porcelain funnel, the asbestos, which serves as a filtering medium, being washed until the wash-water becomes free from platinum. The filtrate is made up to a litre in a measuring flask and 100 c.c. of the solution evaporated three times to dryness with hydrochloric acid on a water-bath. The residue is dissolved in 50 c.c. of hot water containing 5 c.c. of hydrochloric acid, and the silica and any fibres of asbestos filtered off. The filtrate is diluted with water to about 250 c.c. and the platinum precipitated as sulphide, the subsequent procedure being as described above. With a particular sample of platinised asbestos, five estimations of the percentage of platinum present gave results varying from 7·72 to 7·75 by the electrolytic method and from 7·75 to 7·77 by the above hydrogen sulphide method. T. H. P.

Microchemical Estimation of Small Quantities of Platinum in the Presence of Gold and Silver. M. VAN BREUKELEVEEN (*Rec. trav. chim.*, 1917, **36**, 285—288).—A rapid method for estimating the amount of platinum in gold or silver bars. The gold (0·25 gram) is melted with twice its weight of silver, free from platinum, the button being rolled into a thin sheet. This is heated for twenty minutes with 25 c.c. of concentrated sulphuric acid on a sand-bath, the warm acid is decanted, the residue washed with water, and dissolved in the smallest possible quantity of aqua regia. The solution is evaporated to dryness, the residue being further evaporated with a little hydrochloric acid. The final residue is heated at 170—190° for half an hour, the gold being thereby converted into insoluble aurous chloride. To the residue 2 drops (0·1 c.c.) of $N/3$-hydrochloric acid are added, the mixture stirred, and a drop transferred by a loop to a slide and a trace of solid potassium chloride added. After a minute, if platinum is present, yellow octahedra of potassium platinichloride are visible under a microscope. Two more drops of acid are added to the residue, and a second drop removed and examined under the microscope after the addition of potassium chloride. This process is continued until crystals of potassium platinichloride are no longer visible. By working under the same conditions with a gold of known platinum content, it is possible to determine the value of two drops of the $N/3$-hydrochloric acid in terms of platinum percentage in the original alloy. If the alloy under examination is silver with a trace of platinum, then 0·5 gram is used and melted with 0·125 gram of gold free from platinum. W. G.

Estimation of Ethyl Alcohol in Dilute Solutions (0·1 to 1%). Application of the Method to Urine. VILLEDIEU and HÉBERT (*J. Pharm. Chim.*, 1917, [vii], **15**, 41—44).—The iodometric method described depends on the fact that, at a definite dilution, the quantity of alcohol converted into iodoform is constant. Solutions are prepared containing quantities of alcohol varying from

0·1 to 1% of alcohol, and these solutions are treated as follows in order to obtain the value of the silver nitrate solution, used in the final titration, in terms of different quantities of alcohol. One hundred c.c. of the alcoholic solution are treated with 10 c.c. of 16% sodium hydroxide solution, and about 30 c.c. of 10·5% iodine solution are then added drop by drop. After three hours, a further small quantity of iodine solution is added, so that the mixture exhibits a yellow coloration, and, at the end of twenty-four hours, the precipitate is collected and washed with cold water. With the smaller quantities of alcohol it is necessary to seed the mixture with a trace of iodoform in order to promote precipitation. The filter and precipitate are now transferred to a flask, boiled for twenty minutes under a reflux apparatus with 30 c.c. of saturated alcoholic potassium hydroxide solution, the contents of the flask are then acidified with nitric acid, 20 c.c. of $N/100$-silver nitrate solution are added, and the excess of silver nitrate is titrated with $N/100$-thiocyanate solution. The number of c.c. of the silver nitrate solution required to precipitate the potassium iodide formed from the iodoform precipitates in the respective alcoholic solutions is thus obtained, and the numbers correspond with the quantities of alcohol present in the solutions. Any dilute alcoholic solution of unknown strength is treated similarly, and the alcohol content ascertained from the volume of silver nitrate required in the final titration. To estimate alcohol in urine, 200 c.c. of the sample, which must be free from acetone and aldehydes, are distilled after the addition of 1 c.c. of phosphoric acid, and 100 c.c. of distillate are collected and treated as described. W. P. S.

Analytical Differentiation between Fermented Sweet Wines and "Mistelles." W. I. BARAGIOLA and CH. GODET (*Zeitsch. anal. Chem.*, 1916, **55**, 561—577. Compare A., 1903, ii, 689).—Fifteen samples of "mistelles" (wines prepared by adding alcohol to grape juice) and eleven samples of fermented sweet wines were analysed, estimations being made of the quantities of ether-soluble acids, lactic acid, ammoniacal nitrogen, lævulose, dextrose, glycerol, ash, etc., present, but the results obtained show that the present analytical processes do not afford any means of distinguishing between these two classes of wines. W. P. S.

Estimation of Phloroglucinol and Resorcinol by means of Furfuraldehyde. EMIL VOTOČEK (*Ber.*, 1916, **49**, 2546—2547. Compare A., 1916, ii, 542).—An acknowledgment that the essentials of the author's process for the estimation of phloroglucinol were embodied in a paper by Welbel and Zeisel (A., 1895, ii, 426) which he had overlooked. J. C. W.

Colorimetric Methods for Estimating Cholesterol in Serum. PAUL G. WESTON (*J. Biol. Chem.*, 1917, **28**, 383—387). —The author describes a new colorimetric method for the estimation of cholesterol in serum in which the serum is boiled for two hours with 25% potassium hydroxide solution, and is then treated, after concentration, with a saturated solution of calcium hydroxide. The resulting precipitate is collected, dried, and extracted with chloroform, and the extracted cholesterol then estimated by the colour produced on adding sulphuric acid to its solution in chloroform.

Six methods for the estimation of cholesterol are applied to a sample of serum, to a portion of which a known quantity of cholesterol is added. Uniformly consistent results are obtained by the methods of Autenrieth and Funk, Weston and Kent, Csonka, Gettler and Baker, and Weston, whilst Bloor's method yields very variable and inaccurate results. H. W. B.

Analysis of Honey and other Substances containing Lævulose. W. R. G. Atkins (*Analyst*, 1917, **42**, 12—13).—The bromine oxidation method described by Wilson and Atkins (A., 1916, ii, 652) is recommended. An excess of bromine is added to the solution containing dextrose, lævulose, and maltose; sulphuric acid is then introduced in quantity sufficient to render the solution decinormal, and the mixture is shaken for forty-two hours. After this time, the excess of bromine is removed by the addition of sulphurous acid, the solution is nearly neutralised with potassium carbonate, and the reducing power of an aliquot portion is estimated by Kendall's method (A., 1912, ii, 393). Under these conditions of oxidation, a loss of about 1% of the lævulose takes place, but this loss is balanced by the small quantities of dextrose and maltose which remain unaffected. If only dextrose and lævulose are present, as in the case of honey, it is sufficient to estimate the reducing power before and after oxidation. Sucrose, when present, is estimated separately from the reducing power before and after inversion. Oxidation should be made on the inverted solution, allowance being made for the dextrose and lævulose formed from the sucrose. W. P. S.

Estimation of the Volatile Fatty Acids. Colorimetric Qualitative Reactions for their Identification. D. C. Dyer (*J. Biol. Chem.*, 1917, **28**, 445—473).—The method described by the author is one of steam distillation, in which the aqueous solution containing the acid or acids is maintained throughout the course of the distillation at a constant volume of 150 c.c. In these circumstances, the "distilling constants," that is, the percentage amounts of the acid distilled in successive 10 c.c. or 100 c.c. of distillate, when plotted on a logarithmic chart, are indicated by a straight line when only one acid is present, and, in the case of two or more volatile acids, by a curved line which eventually becomes a straight line parallel to the line representing the lowest acid of the series present in the mixture.

For the identification of a single acid by this method, the total amount of acid present is first estimated by titration with standard alkali and the distillation then arranged so that the total 150 c.c. volume in the distilling flask contains about 0·5 c.c. of the pure acid. The acid is now liberated by the addition of an equivalent amount of sulphuric acid, and the distillation with steam commenced. When a convenient amount of distillate, say, 100 c.c., has collected, it is titrated with the standard alkali, and the percentage amount of acid which has distilled thus determined. This constitutes the distilling constant of the acid for the first 100 c.c. of distillate, and reference to the chart immediately reveals the nature of the acid present.

Examples are given showing the application of the method for the estimation of mixtures of two volatile fatty acids; and, in addition, a series of tests is described, depending on the difference in solubility of the iron and copper salts of the acids in various organic solvents, which serves to identify the acids in the distillate and to check the results of the distillation with steam. H. W. B.

Estimation of Free Sulphuric, Nitric, and Picric Acids in the Presence of each other. F. W. RICHARDSON (*J. Soc. Chem. Ind.*, 1917, **36**, 13—15).—The methods described are more particularly intended for the estimation of small quantities of the acids in effluents from picric acid works. The picric acid is estimated colorimetrically in a Lovibond tintometer, the yellow units of this instrument having been standardised previously against solutions containing definite quantities of picric acid. The observations must always be made at the same temperature, since the colour of picric acid solutions varies in depth with change of temperature. The nitric acid is also estimated colorimetrically by means of the phenoldisulphonic acid reaction, the colorations being observed in the tintometer; allowance is made for the colour contributed by the picric acid. The acidity of the three acids together is found by titrating a portion of the water with $N/10$-sodium hydroxide solution, using methyl-red as indicator; the acidity due to the picric and nitric acids is calculated and deducted, and the remaining acidity represents the quantity of sulphuric acid present.

It was found by experiment that waters containing sulphuric acid or nitric acid, or both, attacked iron, and when the water was used in boilers extensive corrosion occurred. Dilute picric acid solution also attacked iron readily. W. P. S.

Detection of Picric Acid and its Derivatives. HENRI PECKER (*J. Pharm. Chim.*, 1917, [vii], **15**, 70—74).—Urine containing picric acid or picramic acid gives a red coloration when rendered ammoniacal and brought into contact with ferrous sulphate–tartaric acid solution. The test gives the best results when made as a ring-test, and will detect the presence of 2 mg. of picric acid or picramic acid per litre of urine. By diluting a urine with definite quantities of water until the reaction is just observable, the quantity of the two acids present may be estimated approximately. The picric and picramic acids may be extracted previously with ether, after the urine has been oxidised; when the two acids are dyed on to wool, the picric acid is more readily extracted from the wool by ammonia than is picramic acid. The diazo-reaction described previously by the author (A., 1916, ii, 353) will detect as little as 0·05 mg. of picramic acid per litre of urine. W. P. S.

Characterisation of Urotropine. P. CARLES (*Ann. Chim. anal.*, 1917, **22**, 8—9).—Urotropine (hexamethylenetetramine) is soluble in water, the solution being neutral to litmus; the substance should be free from chlorides and sulphates, and volatilise completely when heated. A red coloration is obtained when 0·1 gram of hexamethylenetetramine is heated with the addition of 0·1 gram of salicylic acid and 5 c.c. of sulphuric acid. If a 10% solution of hexamethylenetetramine is treated with one-fourth of its volume of sodium hypobromite solution and the mixture then neutralised with hydrochloric acid, a yellow precipitate is formed. W. P. S.

Estimation of Amino-nitrogen in Blood. JOSEPH C. BOCK (*J. Biol. Chem.*, 1917, **28**, 357—368).—The best precipitant for the removal of the proteins of the blood prior to the estimation of the amino-nitrogen is found to be trichloroacetic acid. Alcohol and phosphotungstic acid both give good precipitates, but they appear to retain traces of the amino-acids, so that the filtrates contain less amino-nitrogen than that which is obtained when trichloroacetic acid is employed. H. W. B.

Estimation of Dicyanodiamide in Nitrolime. A. STUTZER (*Zeitsch. angew. Chem.*, 1916, **29**, 417—418).—Since water is an unsuitable medium for extracting nitrolime (compare A., 1916, i, 548), the use of alcohol is recommended. Alcohol dissolves the free cyanamide and the dicyanodiamide completely, whilst only traces of nitrolime pass into solution. Ten grams of the nitrolime should be shaken for two hours with 100 c.c. of 94% alcohol, the mixture then filtered, and the total nitrogen estimated in 20 c.c. of the filtrate. Another portion of 50 c.c. of the filtrate is treated with 180 c.c. of water, 10 c.c. of 10% silver nitrate solution, and 10 c.c. of 10% ammonia; the free cyanamide is thus precipitated as its silver compound and the precipitate is collected on a filter. Two hundred c.c. of the filtrate from this precipitate are then treated with 50 c.c. of 10% sodium hydroxide solution, and, without heating, the precipitated silver dicyanodiamide is collected, washed, and the nitrogen in it is estimated in the usual way. The nitrogen in the silver cyanamide precipitate may also be estimated; this precipitate should not be washed until the filtrate has been collected for the estimation of the dicyanodiamide. The procedure given decreases the loss which takes place when silver dicyanodiamide is heated with sodium hydroxide to expel ammonia. W. P. S.

Impure Picric Acid as a Source of Error in the Estimation of Creatine and Creatinine. OTTO FOLIN and E. A. DOISY (*J. Biol. Chem.*, 1917, **28**, 349—356. Compare Hunter and Campbell, this vol., ii, 110).—The authors find that the observations on Folin's method of creatinine estimation published by McCrudden and Sargent (A., 1916, ii, 358, 587) were obtained by the use of an extraordinarily impure picric acid. When pure picric acid is employed, the irregularities obtained by McCrudden and Sargent do not occur. A method for the preparation of pure picric acid from the commercial material is described, which depends on the repeated salting out of sodium picrate by the addition of sodium chloride to the hot alkaline solution. The picric acid is subsequently liberated from the purified picrate by sulphuric acid.

While the findings of McCrudden and Sargent are abundantly accounted for on the basis of impurities in their picric acid, the fact remains that the yellow colour of pure sodium picrate does limit the dilution in which creatinine may be estimated by the colorimetric method. A modification of the method is therefore described for dilute creatinine solutions in which the excess of picric acid is removed by the addition of a solution containing 7% potassium hydroxide and 25% potassium chloride. Most of the picric acid is precipitated as the potassium salt, and therefore after centrifugalisation the colour due to the creatinine in the clear liquid is made more predominant. The standard creatinine solution must be similarly treated before the comparison is made.

The presence of a second substance of creatinine nature in urine, reported by McCrudden and Sargent (*loc. cit.*), is disproved, and admitted by McCrudden and Sargent to be incorrect. H. W. B.

Sensitive Reaction of the Alkaloids of the Solanaceæ. Anon. (*J. Pharm. Chim.*, 1917, [vii], **15**, 54; from *Pharmazevtizeski J.*, 1916, 263).—An intense reddish-violet coloration is obtained when a trace of an alkaloid from the *Solanaceae* is heated with a drop of a mixture consisting of *p*-dimethylaminobenzaldehyde, 2 grams, concentrated sulphuric acid, 6 grams, and water, 0·4 gram; the reaction may be obtained with 0·0002 mg. of the alkaloids. Atropine, hyoscyamine, and scopolamine behave identically with the reagent. Codeine and morphine yield a red coloration in the cold; quinine, a reddish-brown coloration; eserine and veratrine, green colorations; and narcotine and papaverine, orange colorations. W. P. S.

Preparation of Hide Powder. Y. S. Zalkind and N. I. Egorkin (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 302—304).—The authors describe a method for preparing hide powder suitable for determining the content of tannins in tanning extracts, such powder being difficult to purchase under existing conditions. T. H. P.

General and Physical Chemistry.

New Lines in the Spectrum of Magnesium. Miguel Catalán Sañudo (*Anal. Fis. Quim.*, 1916, **14**, 584—596).—The presence of twelve new lines in the arc spectrum of magnesium in air has been proved, as well as the existence of two different spectra for the metal and its oxide. A. J. W.

Dispersion and the Size of Molecules of Hydrogen, Oxygen, and Nitrogen. L. Silberstein (*Phil. Mag.*, 1917, [vi], **33**, 215—222).—By application of the theory of dispersion the author has calculated the distance between the atoms in the molecules of hydrogen, oxygen, and nitrogen. This method gives $1\cdot067 \times 10^{-8}$ cm. for hydrogen, $1\cdot265 \times 10^{-8}$ cm. for oxygen, and $1\cdot493 \times 10^{-8}$ cm. for nitrogen. Incidentally, it is found that the number of dispersive electrons in the atoms of hydrogen, oxygen, and nitrogen is the same as the normal valency. The above values of the inter-atomic distances are in agreement with the radii of the respective molecules as found by methods based on the kinetic theory. H. M. D.

Absorption-coefficient of Solutions of Cobalt Chloride in Water and various Alcohols for Monochromatic Radiation. E. O. Hulbert, J. F. Hutchinson, and H. C. Jones (*J. Physical Chem.*, 1917, **21**, 150—164).—The authors have carried out a large number of experiments on the absorption of monochromatic light by solutions of cobalt chloride in water, methyl alcohol, ethyl alcohol, propyl alcohol, *iso*butyl alcohol, and *iso*amyl alcohol. The measurements were made at intervals of 20—40 $\mu\mu$ over the range 600 $\mu\mu$—1300 $\mu\mu$, and with solutions of varying concentration at the ordinary temperature. The value of A, the molecular absorption-coefficient, has been calculated from all measurements by the formula $A = (a - a_0)/c$, where a is the absorption-coefficient of the solution, a_0 that of the solvent, and c the molecular concentration. It is shown that in the region of wave-lengths lying on the long wave-length edge of the yellowish-red absorption band the A—c curves show that A decreases with dilution. In the case of aqueous solutions this decrease is considerable, and in the alcoholic solutions the decrease becomes more and more marked the greater the molecular complexity of the alcohol. This is in complete accord with the previously published work of Jones and Anderson (Carnegie Inst. of Washington Publications, No. 110). In the region of low absorption between the two bands A is constant, but in many cases the value of a is so small that deductions as to the value of A are not very trustworthy. In the region of wave-lengths lying on the edge of the infra-red band, A shows variations, and these variations show a regularity which is concomitant with the molecular complexity of the solvent. In this region A is nearly constant for the aqueous solutions, but increases with dilution for the alcohol solutions, the increase becoming greater as the molecular weight of the alcohol increases. In certain cases A decreases to a minimum with dilution and then increases again, but in no case was A found to increase to a maximum and then decrease. At present no theory is advanced to explain these facts, but the fact that A varies with c has probably been correctly attributed by Jones and Anderson (*loc. cit.*) and others to the formation of complexes, which were considered to be loose chemical compounds of molecules of the salt with molecules of the solvent. It is unquestionable that the changes recorded in the present paper may be explained in a qualitative manner by the solvate hypothesis. J. F. S.

Positive Ionisation of certain Hot Salts, together with some Observations on the Electrical Properties of Molybdenite at High Temperatures. A. T. WATERMAN (*Phil. Mag.*, 1917, [vi], **33**, 225—247).—Making use of the method employed by Richardson (A., 1913, ii, 910), the author has examined the positive emission of the following hot salts: silver chloride, silver bromide, lead chloride, lead bromide, cuprous chloride, cupric chloride, aluminium fluoride, platinous chloride, and molybdenite, with the object of ascertaining whether any relationship exists between the valency of the metal and the charges on the ions composing the positive emission. It is shown that silver chloride, silver bromide, lead chloride, lead bromide, platinous chloride, and cupric chloride do not give rise to characteristic positive emissions. The same is probably true for aluminium fluoride. In the case of cuprous chloride there are indications that the ion Cu^{++} is expelled. In nearly every case examined positive ions have been found to be present, for which the value of e/m corresponds with singly charged atoms, either of potassium or of sodium or of both these elements; the results therefore confirm those of Richardson (*loc. cit.*). It is possible that the characteristic emission from these salts does occur, but is too small for measurement with the apparatus used. Molybdenite has been found to possess the following interesting electrical properties. 1. In the range of temperature between the ordinary and a brilliant red heat this mineral exists in two distinct states. 2. The resistance in the low voltage or low temperature state is very nearly an inverse exponential function of the absolute temperature. 3. At the ordinary temperature the resistance is a function of the applied potential difference, and appears to approach an infinite value as the potential approaches zero. 4. The conduction of electricity is evidently carried on by electrons. 5. With regard to the thermo-ionic emission from molybdenite it is noted that a large emission (mainly K^+ emission) takes place from impurities, and that a characteristic emission of Mo^+ ions also occurs, which apparently has no exclusive relationship to the break or to either state. J. F. S.

Chemical Composition versus Electrical Conductivity.

Colin G. Fink (*J. Physical Chem.*, 1917, **21**, 32—36).—The electrical conductivity of mixtures of finely divided substances is a function of the relative size of the constituent particles. Observations made with mixtures of equal weights of finely powdered tungsten and thoria, which were made into rods and fired at 1600° for three hours, show very large differences in the conductivity.

H. M. D.

Some Particular Cases of Current-potential Lines.

A. H. W. Aten (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 653—670).—A theoretical paper, in which the author considers the form of the curve connecting the electrode potential with the current density. Assuming that the ion concentration in the solution outside the diffusion layer is C and the concentration at the electrode is c, the thickness of the diffusion layer being δ, then the quantity of ions passing per second through 1 cm.^{2} of cross-section is given by $D/86400\,.\,(C-c)/\delta$, in which D is the coefficient of diffusion. The charge carried by these ions is equal to the current density d, which is therefore given by $d=1{\cdot}117D(C-c)/\delta$. By substitution in the equation for the electrode potential, this may be written in the form $E=\epsilon+0{\cdot}058/n\,.\,\log(C-d\delta/1{\cdot}117D)$.

For the limiting value $c=0$, the current density has a maximum value given by $d_{max.}=1{\cdot}117DC/\delta$, according to which the limiting current is proportional to the ion concentration of the solution and to the diffusion-coefficient and inversely proportional to the thickness of the diffusion layer.

The theoretical equations are applied in the discussion of experimental results and in the consideration of the influence of the presence of complex or hydrated ions. The case of the discharge of halogen ions at a silver anode is examined in detail. H. M. D.

An Apparatus for Determining Freezing Point Lowering.

R. G. Van Name and W. G. Brown (*Amer. J. Sci.*, 1917, [iv], **43**, 110—114).—The containing vessel consists of a vacuum-walled tube of about 500 c.c. capacity, surrounded by a projecting jacket of tin and closed by a cork perforated to admit the Beckmann thermometer, the stem of the glass stirrer, a short tube through which the liquid may be inoculated, and a cooling tube.

The cooling tube represents the chief novelty in the apparatus. It consists of two concentric glass tubes through which cold brine is circulated, the cooling liquid passing down the inner tube and up between the inner and outer tubes, whence it emerges through a side-tube. When the desired degree of undercooling has been obtained, the inner tube is lowered so as to close the end of this tube, and this movement uncovers a hole in the upper part of the inner tube, with the result that the brine only circulates through the upper portion of the cooling tube which projects from the apparatus. To prevent the deposition of hoar frost on the part of the cooling tube above the level of the liquid, the upper portion of this tube, down to a point below the surface of the liquid, is surrounded by a narrow vacuum jacket. This arrangement permits the employment of a much colder brine for cooling purposes and increases the rapidity of the freezing-point determination.

Data are recorded for solutions of sucrose, which show that the apparatus yields concordant and satisfactory results. H. M. D.

The Relation of Oxygen to the Heat of Combustion of Organic Compounds. W. M. Thornton (*Phil. Mag.*, 1917, [vi], **33**, 196—203).—If H is the heat of combustion and n the number of oxygen atoms required for the complete combustion of an organic compound, the value of H/n is found to be more or less independent of the nature of the compound. The mean value of H/n according to the data for paraffin, unsaturated and aromatic hydrocarbons, halogen compounds, ethers and acetals, alcohols, aldehydes and ketones, acids, esters, mercaptans, sulphides, thiocyanates, cyanogen, hydrogen cyanide, nitriles, and amines is equal to 53.

The nitro-compounds are anomalous in that H/n has a higher value, but if n is taken to represent the oxygen which is required to burn the carbon and hydrogen, the value of H/n is in agreement with the above mean. This would seem to show that the oxygen in these nitro-compounds takes no part in the combustion process, and this may be due to the difficulty of activating the oxygen when associated with nitrogen so that the combustion is effected by free oxygen.

From the relation $H=53n$, it is possible to calculate the quantity of air required for the combustion of any hydrocarbon mixture of unknown composition if the heat of combustion and the vapour density are known. Conversely, if the calorific value of any liquid or gaseous fuel is required, it may be calculated from the volume of air which is required to burn completely a measured volume of the vapour of known density. H. M. D.

Heat of Dilution of Alcohol in Benzene. Willis A. Gibbons (*J. Physical Chem.*, 1917, **21**, 48—74).—In applying the formulæ for the changes in the vapour pressure, freezing point, and boiling point produced by a solute to calculate the molecular weight of the latter, it is customary to ignore the influence of the heat of dilution. According to Beckmann's determinations (A., 1889, 11) of the molecular weight of ethyl alcohol in benzene solution by the freezing-point method, the molecular weight increases from the normal value in dilute solution to a value about seven times as large in concentrated solution. The heat of dilution in this case is very large, and with the object of determining the connexion between the heat of dilution and abnormal changes in the vapour pressure, the author has made a detailed investigation of the variation of the heat of dilution with the concentration by experiments with solutions of alcohol in benzene.

The apparatus used was an isothermal calorimeter, the use of which minimises the errors which are peculiar to the ordinary calorimeter and avoids also a correction for water equivalent.

Observations were made at 10°, 20°, and 30°, and it is found that the results may be expressed by a formula of the type $x = -(bQ^2 + cQ)/(Q - a)$, in which a, b, and c are constants, Q is the molecular heat of dilution, and x is the number of mols. of solvent (benzene) per mol. of solute (alcohol). The minus sign denotes the fact that heat is absorbed in the dilution of the solutions.

In the final part of the paper an attempt is made to apply the results as a correction to the ordinary molecular weight formula, but the results obtained lead to the conclusion that the theoretical relations are not sufficiently developed to permit of this being done in a proper manner. It seems, however, that the molecular weight will always be too large when heat is absorbed on dilution and too small when dilution is accompanied by development of heat

H. M. D.

Relationship between the Physical Properties of Isomeric Cobaltammines and the Electro-valencies of their Co-ordination Complexes. Rajendra Lal De (T., 1917, **111**, 51—54).—In order to ascertain the influence of electro-valency on the volume occupied by a substance, the author has determined the densities of the isomerides: triamminecobalt nitrate, dinitrotetra-amminecobalti–tetranitrodiamminecobaltiate, and hexa-amminecobalti–hexanitrocobaltiate, the electro-valencies of which are respectively zero, one, and three. The molecular volume at 32—33° increases with the electro-valency, the two increments being nearly equal. The two stereoisomeric forms 1:2 and 1:6 of the second isomeride have the same molecular volume.

The solubilities of the isomerides in water at the ordinary temperature were also determined. Of the two stereoisomeric forms of the second compound, the 1:2 compound is 9·3 times as soluble as the 1:6 form. The influence of spacial configuration on the solubility seems to be of more importance than the electro-valency.

H. M. D.

Molecular Attraction. XIII. J. E. Mills (*J. Physical Chem.*, 1917, **21**, 101—106).—Polemical against Matthews (A., 1916, ii, 600); it is shown that Matthews in his discussion of the Dietrici, Mills, and van der Waals's equations simply substitutes for the internal pressure term (a/v^2) in the van der Waals equation, the more correct expressions derived by the author. Consequently, his conclusions with regard to these equations are incorrect. A number of other errors are pointed out. It is also shown that these errors do not in any way invalidate the discussion or the results arrived at from the relationships of Goldhammer and Eötvos on the attractive forces of the molecules.

J. F. S.

The Detergent Action of Soap. Spencer Umfreville Pickering (T., 1917, **111**, 86—101).—Although the detergent action of soap is partly due to its power of emulsifying oil and partly to the low value of the surface tension between oil and soap solution, it seems probable that the detergent effect is influenced to a greater extent by the solubility of oil in soap solutions.

The behaviour of paraffin oil and benzene towards various soaps in admixture with varying quantities of water has been examined, and these observations lead to the conclusion that soluble compounds of oil and soap are formed which are not decomposed by the addition of further water. If the soap is diluted previous to its treatment with oil, the extent to which combination occurs is much smaller, the reduction being attributable to the increase in the emulsification of the oil. The nature of the resulting system varies from a limpid liquid compound to an almost solid emulsion. The proportions in which oil and soap combine together depend on the chemical as well as the physical nature of the reagents.

Experiments made with naphthalene and soap show that this hydrocarbon behaves quite differently from paraffin oil. It dissolves to a small extent in heated soap, but some of this crystallises out on cooling. The solubility is increased by the addition of a little water, but diminishes on further dilution. In presence of naphthalene, the quantity of paraffin oil dissolved by soap diminishes. H. M. D.

Crystallography and Röntgen Rays. M. von Laue (*Ber.*, 1917, **50**, 8—20).—A lecture delivered before the German Chemical Society on November 11th, 1916, dealing with the space-lattice structure of crystals. J. C. W.

The Ultimate Structure of Crystals. F. Rinne, (*Jahrb. Min.*, 1916, ii, 47—108).—A theoretical paper in which the author discusses the recent application of *X*-rays to the study of crystals. Alongside the science of stereochemistry is developing a stereophysics, and these, together with the study of crystal structure, form a new branch of science, which the author terms "Feinbaulehre der Materie" (the study of the ultimate structure of matter), or Leptonology (λεπτός). Whether the crystal be considered as an atomic structure, or as containing groups of atoms or molecules, the influence of electrons on the structure must soon be brought under consideration. Debye has already studied the constitution of the hydrogen molecule (*Ber. Akad. München*, 1915) and of the liquid benzene molecule (Debye and Scherrer, *Nachr. Ges. Wiss. Göttingen Math.-phys. Kl.*, 1916) by means of *X*-rays. The diameter of the benzene molecule he finds to be $12{\cdot}4 \times 10^{-8}$ cm. and its thickness at most $1{\cdot}9 \times 10^{-8}$ cm. The different forms of matter, gas, liquid, liquid crystal, and crystal form a continuous series, and each in turn is discussed by the author. In liquid crystals, the particles are orientated regularly with respect to one axis. It is suggested that the molecules become orientated with their principal axes parallel, giving a close approximation to an optically uniaxial crystal (compare this vol., ii, 18). The growth of a crystal is attributed to the special properties of the surface layer. The atoms in the superficial zone of imperfectly crystalline material have some of their valencies unsaturated, whereby fresh material can be attracted.

A considerable number of Laue diagrams are included in the paper, illustrative of olivine, sucrose, cordierite, oligoclase, muscovite, aragonite, calcspar, albite, and anorthite, and are employed in a discussion of the phenomena of isomorphism, polymorphism, and morphotropy. E. H. R.

The Reversibility of Sulphide Sols and the Protective Action of Hydrogen Sulphide. S. W. YOUNG and WIN R. GODDARD (*J. Physical Chem.*, 1917, **21**, 1—13).—A dialysing apparatus is described which has been employed in the investigation of the influence of hydrogen sulphide on the stability of colloidal solutions of metallic sulphides. The results obtained with cadmium, zinc, lead, arsenic, and mercuric sulphides show that the removal of hydrogen sulphide by dialysis causes coagulation of the metallic sulphide, but that the coagulated sol is redispersed when hydrogen is again introduced into the solution. It would seem that the coagulation and dispersion are determined by the concentration of the hydrogen sulphide.

In experiments made with zinc sulphide, it was found that the dispersive power of the hydrogen sulphide increases up to a pressure of 1·5—2 atmospheres, and then decreases somewhat as the pressure is further increased. The dispersive power of hydrogen sulphide is also shown by the results of experiments in which potassium chloride in varying quantities was added to the colloidal zinc sulphide. The coagulate obtained by raising the temperature of the sol is also dispersed under the influence of hydrogen sulphide.

H. M. D.

Colloidal Solutions of Copper Sulphide. S. W. YOUNG and ROLAND NEAL (*J. Physical Chem.*, 1917, **21**, 14—31).—The properties of copper sulphide sols have been examined, the experiments being designed to show the influence of electrolytes and of hydrogen sulphide on the coagulation of the sols and on the mobility of the colloidal particles.

Colloidal solutions were prepared by the agitation of well-washed copper hydroxide, copper carbonate, or freshly precipitated copper sulphide with aqueous hydrogen sulphide. The coagulation experiments show that the concentration of a given electrolyte, which is required to produce coagulation within twenty-four hours, is independent of the mode of preparation of the sol, of the presence or absence of free hydrogen sulphide, and within wide limits is independent of the concentration of the colloidal solution. The relative coagulating powers of the chlorides of potassium, calcium, and aluminium are as 1 : 39 : 875. Sols which have been freed from hydrogen sulphide are unstable, and when kept for some months undergo spontaneous coagulation, but so far as the influence of electrolytes is concerned, the behaviour of the sols is the same whether hydrogen sulphide is present or not.

The mobility of the colloidal particles in an electric field varies according to the mode of preparation. The mobility is increased in the presence of electrolytes, but the increase bears no apparent relation to the coagulating power of the electrolyte used. On the other hand, the increase in the mobility seems to depend on the mobility of the particles in the original sol. The mobility of the particles of a particular sol increases with the dilution, and is greatly reduced by hydrogen sulphide. Removal of the hydrogen sulphide restores the sol to its original condition, and the change is therefore reversible. The effect produced by bubbling air or oxygen through the sol can be entirely explained by the removal of hydrogen sulphide.

It is suggested that the formation of colloidal solutions of copper sulphide may play a part in the processes which are involved in the secondary enrichment of gels of copper sulphide ore.

H. M. D.

The Action of Mercuric Chloride on Gold Hydrosols. O. Herstad (*Koll. Chem. Beihefte*, 1916, **8**, 399—424).—According to previous observations, the coagulating power of mercuric chloride towards gold sols is greater than that of most salts of the heavy metals. The action does not occur if hydrochloric acid is added to the mercuric chloride solution. In view of the fact that mercuric chloride is only slightly ionised, its behaviour is rather remarkable, and a further examination of the phenomena has been undertaken with colloidal gold solutions prepared by the action of formaldehyde.

These experiments show that coagulation of gold sols by mercuric chloride is inhibited by the addition of acid, and the effect is also not observed if the sol is dialysed or boiled before the mercuric chloride is added. By means of electrometric measurements, it has been found that coagulation only occurs in the case of sols which are slightly alkaline. The hydrion concentration, which is sufficient to prevent coagulation, varies with the concentration of the mercuric chloride. For a given hydrion concentration, there is an upper as well as a lower limiting value of the mercuric chloride concentration which produces coagulation, and if a diagram is constructed by plotting hydrochloric acid concentration on the abscissa and mercuric chloride concentration on the ordinate, the coagulating mixtures fall within a zone which is bounded by the ordinate and by two intersecting curves which represent the upper and lower limiting values of the mercuric chloride concentration.

It is supposed that the coagulating power of mercuric chloride is due to mercuric oxide (or mercurous oxide), which forms an envelope round the colloidal gold particles and transforms the negative colloid into a positive colloid.

The gold sols afford evidence of ageing in that they gradually become less sensitive to mercuric chloride, and this is supposed to be the result of a slow oxidation of the gold by the formaldehyde present.

H. M. D.

Protective Colloids. VII. Cydonia Seed as Protective Colloid. II. Colloidal Silver. A. Gutbier and A. Wagner (*Kolloid Zeitsch.*, 1916, **19**, 280—287. Compare this vol., ii, 131). —The action of quince seed extract as a protective colloid has been examined in experiments with silver sols prepared by the reduction of silver nitrate by hydrazine hydrate in presence of the organic colloid. By dialysing the resulting colloidal silver solution and evaporating at low temperature or precipitating by the addition of alcohol, solid substances have been obtained containing about 20% of silver, which dissolve completely in water.

Reversible colloids of the same kind were also obtained by the action of sunlight on silver nitrate solutions in presence of the quince seed extract. The coagulation of these protected silver sols by the action of various electrolytes has been examined, and the results indicate that the coagulating power diminishes in the order: sulphuric acid, sodium chloride, sodium carbonate, sodium hydroxide. H. M. D.

Protective Colloids. VII. Cydonia Seed as Protective Colloid. III. Colloidal Gold. A. Gutbier and A. Wagner (*Kolloid Zeitsch.*, 1916, **19**, 287—291).—Experiments similar to those recorded in the previous paper have shown that solid substances which contain up to 50% of gold and are completely soluble in water may be obtained by the reduction of gold chloride by hydrazine hydrate in presence of quince seed extract. The protective action of the organic colloid on the gold sols is very pronounced. H. M. D.

Protective Colloids. VII. Cydonia Seed as Protective Colloid. IV. Colloidal Mercury. A. Gutbier and A. Wagner (*Kolloid Zeitsch.*, 1916, **19**, 291—297).—The protective action of quince seed extract on colloidal solutions of mercury prepared by the action of hydrazine hydrate on mercuric chloride is not very marked. If, however, sodium hyposulphite is used as the reducing agent, much more stable solutions are obtained, and by dialysing and evaporating or precipitating with alcohol, solid colloids containing up to about 20% of metallic mercury have been prepared which are partly soluble in water. H. M. D.

Protective Colloids. VII. Cydonia Seed as Protective Colloid. V. Colloidal Platinum. A. Gutbier and A. Wagner (*Kolloid Zeitsch.*, 1916, **19**, 298—302).—Platinum sols, prepared by the reducing action of hydrazine hydrate on platinum chloride in presence of quince seed extract, yield, on dialysing and evaporating or precipitating by the addition of alcohol, solid colloidal substances which contain as much as 25% of platinum. These colloids are readily soluble in warm water. As in the case of silver, gold, and mercury, the protective action of quince seed extract on colloidal platinum is strongly marked. The coagulation phenomena associated with the presence of electrolytes has also been examined. H. M. D.

Non-, Uni- and Bi-variant Equilibria. XI. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 713—727. Compare this vol., ii, 132).—A further theoretical consideration of the equilibrium relations in binary systems with two indifferent phases. For any binary system in which two indifferent phases occur there are two types of pressure–temperature diagram, and the author shows how these may be derived. H. M. D.

The Influence of Temperature on Chemical Equilibria. F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 636—649).—The integration of the equation $d \log K / dT = Q / RT^2$ leads to various formulæ expressing the connexion between the equilibrium constant of a reversible chemical change and the temperature, the nature of which depends on the assumed relation between the heat of reaction, Q, and the temperature, T. If the algebraic sum of the heat capacities of the systems on the two sides of the equation is zero at all temperatures, the integrated equation is of the form $\log K = a/T + b$, in which a and b are constants.

The author maintains that this equation is in satisfactory agreement with the experimental data for many gas reactions. Although for such systems the algebraic sum of the heat capacities of the reacting substances is not in general equal to zero, yet the influence of this factor is in most cases so small that the error which is involved in the assumption of the zero value is not nearly so large as the errors incidental to the equilibrium measurements. On this account it is claimed that the above equation is to be preferred to the more complicated expressions which are frequently used to represent the variation of the position of chemical equilibrium with the temperature.

The validity of the argument is supported by a comparison of the values of log K afforded by the experimental data for the reactions $2CO_2 \rightleftharpoons 2CO + O_2$ and $2HI \rightleftharpoons H_2 + I_2$ with those which have been calculated from the simple equation and from more complicated expressions.

Reactions in which solid substances take part may be expected to show greater deviations from the requirements of the simple formula. In this connexion the author has examined the data corresponding with the equilibria $Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2$, $FeO + CO \rightleftharpoons Fe + CO_2$, and $Fe_3O_4 + 4CO \rightleftharpoons 3Fe + 4CO_2$, and comes to the conclusion that the available data are untrustworthy. According to Bauer and Glässner (A., 1903, ii, 423), the curve for the equilibrium $FeO + CO \rightleftharpoons Fe + CO_2$ shows a minimum at 680°. At this temperature the heat of reaction is zero, whereas at 585° it is -3114 cal. and $+8724$ cal. at 835°. The heat of reaction, according to this, changes to the extent of 11,838 cal. for a change of temperature of 250°. This would correspond with a value of 47·3 cal. for the algebraic sum of the heat capacities of the reacting substances, a value which is much too large to be accepted as possible. Similar relations are found when the data for the other equilibria are examined, and for this reason the author considers that the recorded numbers are not nearly so accurate as has been assumed.

A further case of equilibrium examined is the dissociation of ammonium bromide, the constant for which, according to Smith and Lombard (A., 1915, ii, 86), shows a maximum at about 320°.

At higher temperatures heat is apparently developed in the dissociation process, and at 384° the calculated heat of reaction is 43,000 cal. This change in the heat of reaction for a temperature variation of 64° corresponds with a value of 670 cal. for the algebraic sum of the heat capacities of the ammonium bromide and its dissociation products. This value is much too large, and suggests that the experimental observations are inaccurate.

In the present state of our knowledge of gas equilibria it would therefore seem that the influence of temperature may be adequately represented by means of the formula which neglects the differences in the heat capacities of the reacting systems. H. M. D.

Influence of the Solvent on the Situation of the Homogeneous Equilibrium. A. Smits (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 708—712).—There is a great deal of evidence to show that the equilibrium which is set up between the substances involved in a reversible reaction varies with the nature of the solvent. This variation has not yet been satisfactorily explained, but the author shows by theoretical reasoning that the shift in the position of equilibrium in passing from one solvent to another must be ascribed to a difference in the heat of the reaction in the two solvents. This in its turn may be referred to differences in the heats of dissolution of the reacting substances in the solvents in question. If the reversible reaction is represented by $A \rightleftharpoons B$ and Q_A and Q_A' are the heats of dissolution of A in two different solvents, the corresponding heats of dissolution of B being Q_B and Q_B', then the relation between the equilibrium constants K and K' is given by $\log K/K' = \{(Q_A - Q_A') - (Q_B - Q_B')\}/RT$. H. M. D.

"Stepped" Ignition. Richard Vernon Wheeler (T., 1917, **111**, 130—138).—The ignition of inflammable mixtures of gases by the impulsive electrical discharge is stated by Thornton (A., 1914, ii, 524, 834) to be characterised by discontinuities which are observed when the composition of the mixture is varied at constant pressure or when a given gas mixture is examined under varying pressure.

Using a method of experiment of the same kind, the author has been unable to detect any discontinuity in the ignition of a 9·5% mixture of methane and air when the pressure was varied from 100 to 800 mm. The curves obtained by plotting the "igniting-currents" against the pressure are quite continuous. It would seem that the results obtained by Thornton require some condition of experiment which the author has been unable to reproduce or has been careful to exclude.

[With Allan Greenwell.]—A mathematical analysis of the hyperbolic curve suggests that the quantities actually recorded are not really independent. The independent variables, as distinguished from the recorded variables, may be represented by employing inclined axes parallel to the asymptotes of the hyperbola, the origin remaining the same. The distance between the new ordinate and the relative asymptote represents the minimum ignition pressure for any value of the current and the distance between the new abscissa and the relative asymptote gives the minimum igniting current for any degree of compression. The product of the real pressure minus the minimum pressure and the real igniting current minus the minimum igniting current is constant.

H. M. D.

Limits of Inflammability of Gaseous Mixtures. W. M. THORNTON (*Phil. Mag.*, 1917, [vi], **33**, 190—196).—According to previous experiments (compare A., 1914, ii, 834), the curve expressing the relation between the energy of the igniting current in impulsive spark or condenser discharge and the composition of a mixture of inflammable gas and air shows marked discontinuities for certain mixtures which are characterised by the fact that the ratio of the oxygen atoms to the molecules of inflammable gas is represented by a whole number. It is now shown that simple relations of the same kind are exhibited by the mixtures which correspond with the upper and lower limits of inflammability.

In the upper limit mixtures of the paraffin hydrocarbons there is twice as much inflammable gas as in that which corresponds with perfect combustion. In the case of acetylene, cyanogen, and carbon disulphide this ratio is equal to three, whilst for hydrogen it is five, and for carbon monoxide it is equal to six.

In respect of the lower limit of inflammability it is found that in the case of the hydrocarbons, ignition fails when the mixture contains twice as much oxygen as is required for complete combustion. If n is the number of oxygen atoms required for the combustion of one molecule of inflammable gas, the lower limiting mixture contains $2n-1$ atoms of oxygen. The ratio of the oxygen atoms in the lower limiting mixture to the normal number of oxygen atoms is, on the other hand, $(3n-2)/n$ for methyl alcohol, ethyl alcohol, acetylene, cyanogen, and carbon disulphide, $(n+1)/n$ for ethylene, 3 for hydrogen sulphide and carbon monoxide, and 9 for hydrogen.

If U is the percentage of inflammable gas in the upper limiting mixture, then $U \times n$ is approximately constant. Similarly, if L is the percentage of inflammable gas in the lower limiting mixture and n_L is the number of oxygen atoms per molecule of inflammable gas in this mixture, it is found that $L \times n_L$ is very nearly constant.

Since n is approximately proportional to the heat of combustion of the inflammable gas, it follows that the heat of combustion of unit volume is the same for all upper limit mixtures of inflammable gases. From the constancy of $L \times n_L$ it is also apparent that the number of oxygen atoms in unit volume of the lower limiting mixtures is the same for all inflammable gases.

Since $U \times n$ and $L \times n_L$ are constant, and n/n_L is approximately constant for homologous series of gases, it follows that the ratio of U/L should be nearly constant. The data for the paraffins show that this ratio increases slightly as the series is ascended, and remains constant in the ethylene series.

According to the above data, inflammation is determined by the existence of certain numerical relations between the number of molecules of oxygen and of the inflammable gas, and it would seem that the upper and lower limits of inflammability are controlled by the heat liberated in the reaction. H. M. D.

Valency Centres. O. Hinsberg (*J. pr. Chem.*, 1916, [ii], **94**, 179—192).—A theoretical paper, in which the conception of different centres from which the forces of valency emanate is extended from the case of sulphur (A., 1916, i, 725) to account for many peculiarities of the oxygen, selenium, tellurium, nitrogen, or halogen atom. In general terms it is pointed out that elements with only one valency centre in the atom (for example, carbon) give neutral hydrides, but the acid nature of the hydrides and the basic nature of the onium compounds increase with the number of valency centres. Thus, sulphur and nitrogen, with two centres, give feebly acidic hydrides (H_2S and NH_3) and strongly basic onium compounds; iodine, with three centres, gives a strongly acid hydride and very strongly basic diaryliodonium hydroxides.
J. C. W.

New Laboratory Apparatus for the Evolution of Gas. B. Angeli (*Boll. chim. farm.*, 1917, **56**, 2—3).—A modified Kipp apparatus is described, which functions with a small quantity of the reacting liquid, uses liquid always of the same purity, is easily dismounted, and has other advantages. Two forms are figured.
T. H. P.

Inorganic Chemistry.

The Allotropy of Phosphorus. J. W. Terwen (*Chem. Weekblad*, 1917, **14**, 180—197).—A review of the progress made in the chemistry of phosphorus during the last fifteen years, with a summary of the literature. A. J. W.

Combinations of Arsenious Oxide and Salts. I. and II. F. A. H. Schreinemakers and (Mej.) W. C. de Baat (*Chem. Weekblad*, 1917, **14**, 141—146, 203—208).—An application of Schreinemakers's graphic method to systems containing water and arsenious oxide with the bromides of lithium, sodium, potassium, and ammonium, and lithium chloride, potassium iodide, and the chlorides and bromides of calcium, barium, and strontium.
A. J. W.

Density of Silicon Tetrafluoride. Albert F. O. Germann and Harold S. Booth (*J. Physical Chem.*, 1917, **21**, 81—100).—The authors have determined the density of silicon tetrafluoride which has been subjected to very careful purification. The gas was prepared in a perfectly dry, evacuated apparatus in the usual way from calcium fluoride, silica, and sulphuric acid, and was led over glass wool to remove free hydrogen fluoride and over a column of phosphoric oxide. The gas thus dried was led into a receiver cooled by liquid air and solidified. The product was then melted and fractionally distilled at normal pressure and atmospheric temperature, and after several distillations led into weighed globes and weighed. The author points out that fractional sublimation under reduced pressure, as employed by Jaquerod and Tourpaian (A., 1913, ii, 401, 772), gives a product which is heavier than the product obtained in the present work by two parts per thousand. This is attributed to the presence of the sesquifluoride, Si_4F_6, due no doubt to the fact that Jaquerod and Tourpaian heated the reaction mixture in the preparation of the fluoride, whereas the present authors generated the gas without heat. The weighings were corrected for: (1) the contraction of the evacuated globes; (2) the buoyancy of the air on the weights and globes; (3) for the altitude and latitude; and (4) for the compressibility of the tetrafluoride. As the mean of eleven experiments, it is found that the weight of the normal litre of silicon tetrafluoride is $L_N = 4{\cdot}68397$ grams, which, since the fifth decimal is somewhat doubtful, may be taken as $L_N = 4{\cdot}6840$. J. F. S.

The System-Mercury Iodide. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 703—708).—Red mercuric iodide is transformed into the yellow modification at 127°. When this is heated further, it remains yellow up to about 190°, and then assumes a red tint, which deepens until the substance melts to a dark red liquid at 255·5°. Observations made with large crystals of yellow mercuric iodide show that the gradual development of the orange colour with rise of temperature is not accompanied by any change in the crystalline form. This fact points to the formation of mixed rhombic crystals containing both the yellow and red modifications, the proportion of the latter increasing with rise of temperature. It is suggested that there are two isomeric forms of mercuric iodide (α and β), and that the red and yellow modifications are mixed crystals containing the two forms in different proportions. The equilibrium relationships are examined from this point of view and represented on a temperature-concentration diagram. H. M. D.

The Luminescence of the Iodide of Millon's Base. HARRY B. WEISER (*J. Physical Chem.*, 1917, **21**, 37—47).—When the substance obtained by the action of ammonia on an alkaline solution of mercuric potassium iodide is heated, it decomposes, with the emission of violet light. The products formed are ammonia, mercuric iodide, nitrogen, water, and mercury. Ammonia is evolved at 160°, but the decomposition is not rapid below about 400°. The chemi-luminescence is associated with the rapid decomposition, the reaction being endothermic.

There are apparently three distinct luminescent effects in which mercury or its compounds are involved. It is suggested that the orange luminescence is attributable to the change of the mercurous ion into non-ionised mercurous salt, the green luminescence to the change of mercurous ion into mercuric ion, and the violet luminescence to the conversion of mercuric ion into the mercury atom.

H. M. D.

The Action of Potassium Permanganate on the Metals. William Foster (*Chem. News*, 1917, **115**, 73).—The reduction of potassium permanganate solution by hydrogen in presence of platinum black is sometimes shown as a lecture experiment. Neutral dilute solutions are reduced by many metals, including gold and platinum, even without hydrogen. The solution becomes alkaline, showing the formation of potassium hydroxide, and in some cases the formation of manganate may be observed. Silver reduces quickly, whilst tungsten acts rapidly, but yields a neutral solution. Mercury acts very rapidly, the metal being oxidised (compare Giles, *Chem. News*, 1867, **15**, 204; Borar, T., 1911, **99**, 1414).

C. H. D.

Atmospheric Corrosion of Commercial Sheet Iron. E. A. Richardson and L. T. Richardson (*Chem. News*, 1917, **115**, 62—65).—Two sets of specimens have been used for the comparative tests, one being in the condition as received, and the other annealed and then cleaned from scale by pickling in dilute sulphuric acid, washing and drying, and rubbing with emery. Ten similar specimens of each metal are used for the test, and are placed in a rack exposed to the atmosphere, in a place fairly free from acid fumes. A specimen is considered to have failed when it can be seen to be perforated when the rust is removed by tapping with a blunt object, the thickness of the sheets being in all cases 26 gauge.

The character of the coating of rust varies greatly with the composition of the steel. Bessemer and open-hearth steels form a loose, yellow rust, the other varieties forming a dark red, adherent deposit. The adherence is a maximum in the copper steels, which form a very dark, fine-grained rust. The period of resistance varies from about 350 days for mild steel in the given conditions to more than 1200 days for iron and steel containing copper, these specimens not having failed at the time of the report. The proportion of copper ranges from 0·181 to 0·268%. Charcoal iron and commercial pure iron resist better than mild steel, and the superior resistance of wrought iron is attributed to its greater purity rather than to the presence of slag. Copper has a greater effect on the resistance of steel than on that of iron.

C. H. D.

Some Problems of the Oxides of Iron. Robert B. Sosman (*J. Washington Acad. Sci.*, 1917, **7**, 55—72).—Ferrous oxide has never been obtained in a pure state, and from the analogy of iridium, it is possible that FeO may have a higher dissociation pressure than Fe_3O_4, which would explain the frequent presence of metallic iron and the magnetic oxide in the products of oxidation or reduction. The presence of metallic iron in basic rocks in Greenland may be due to the dissociation of a complex ferrous silicate in this way. Ferrous and ferric oxides form a continuous series of solid solutions.

The magnetic properties of the iron oxides and the geological relations of the oxides are also discussed. C. H. D.

The System H_2O—Bi_2O_3—HCl at 30°. W. JACOBS (*Chem. Weekblad*, 1917, **14**, 208—212).—An investigation by the graphic method of systems made up of bismuth trioxide and aqueous solutions of hydrochloric acid. A. J. W.

Mineralogical Chemistry.

Oceanic Salt Deposits. J. D'ANS, with A. BERTSCH and A. GESSNER (*Zeitsch. Kali.*, 1915, **9**, 148—154, 161—168, 177—183, 193—200, 217—222, 229—236, 245—250, 261—270; from *Jahrb. Min.*, 1916, ii, Ref., 154—156).—Continuing the work of van't Hoff, the authors have (1) investigated anew the whole of the simple ternary and quaternary systems; (2) determined the isotherms for these systems at 0° and 55°, van't Hoff's having been determined at 25° and 83°; (3) investigated the range of existence of calcium sulphate. The complete investigation of the non-variant points is reserved to a later date. Microscopic methods were found to be of great assistance in the research. By means of tables and diagrams the new results are compared critically with those of earlier investigations.

The following systems are dealt with: (1) $KCl-NaCl-H_2O$; (2) $NaCl-MgCl_2-H_2O$; (3) $KCl-MgCl_2-H_2O$; (4) $NaCl-KCl-MgCl_2-H_2O$; (5) $Na_2SO_4-NaCl-H_2O$; (6) $K_2SO_4-KCl-H_2O$; (7) $Na_2SO_4-K_2SO_4-H_2O$; (8) the reciprocal salt pair, $K_2SO_4+2NaCl \rightleftharpoons Na_2SO_4+2KCl$; (9) $MgSO_4-MgCl_2-H_2O$; (10) $Na_2SO_4-MgSO_4-H_2O$; (11) the reciprocal salt pair, $Na_2SO_4+MgCl_2 \rightleftharpoons 2NaCl+MgSO_4$; (12) $K_2SO_4-MgSO_4-H_2O$; (13) the reciprocal salt pair, $K_2SO_4+MgCl_2 \rightleftharpoons 2KCl+MgSO_4$; (14) $Na_2SO_4-K_2SO_4-MgSO_4-H_2O$.

In a sodium-free system containing the components K_2, Mg, SO_4, Cl_2, and H_2O it is found that kainite is not formed below about 13°, but can only exist in contact with the solution between 13° and 85°.

In the complete system of the chlorides and sulphates of sodium, potassium, and magnesium with water, solubility diagrams at 0° and 55° for complete saturation with sodium chloride have been obtained. The results are represented by means of the projection of a solid figure, the three co-ordinates being the quantities of

K_2, Mg, and SO_4 per 1000 mols. H_2O. The increase of solubility with solutions rich in magnesium chloride is clearly shown.

The conditions of formation of the calcium sulphate salts anhydrite, gypsum, glauberite, syngenite, pentacalcium sulphate, $K_2SO_4,5CaSO_4,H_2O$, and polyhalite were also determined. Experimental difficulties were encountered in the form of hysteresis effects, especially in the case of anhydrite. In the space diagrams given, the calcium salt fields are well shown for solutions saturated with sodium chloride.

The crystallisation of sea water at 0°, 25°, 55°, and 83° was studied, on the supposition that complete equilibrium was attained, and the results of these experiments are compared with the natural salt deposits. These deposits are considerably poorer in magnesium than would be expected from the experiments, and it is probable that magnesium chloride has been dissolved out. Probably the deposits were first formed at 25—30°, but there must subsequently have been a considerable rise of temperature.

E. H. R.

Identity of Hamlinite with Goyazite. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1917, [iv], **43**, 163—164).—A tabulation of the characters, so far as determined, of goyazite from Brazil (Damour, 1884) and of hamlinite from Maine and Switzerland (Hidden and Penfield, 1890) suggests the identity of these minerals; or, at least, their essential difference remains to be proved. The material is a hydrous phosphate of aluminium and strontium crystallising in the rhombohedral system and belonging to the alunite–beudantite group of minerals.

L. J. S.

Two so-called Halloysites from Georgia and Alabama. P. A. VANDER MEULEN (*Amer. J. Sci.*, 1917, [iv], **43**, 140—144).—Analysis I is of a sedimentary clay, possessing the external characters of halloysite, and hitherto referred to that species, from Chattooga County, Georgia; and II of similar material from the Fort Paine chert formation in northern Alabama. They contain less water and more alumina and have a higher density than halloysite ($Al_2O_3,2SiO_2,2H_2O + aq.$), and they are probably mixtures of kaolinite ($Al_2O_3,2SiO_2,2H_2O$) and gibbsite ($Al_2O_3,3H_2O$), containing respectively 21·32% and 4·83% of gibbsite. Minute, acicular crystals of gibbsite were detected on crevices in the Georgia clay. The presence of gibbsite in greater amount in I is also suggested by the fact that more water is lost at 300° than from II, and that dilute sulphuric acid extracts more alumina:

	SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	Na_2O.	H_2O 108°.	H_2O >108°.	Total.	Sp. gr.
I.	35·82	44·38	trace	trace	1·18	1·61	16·63	99·62	2·497
II.	43·30	39·94	trace	0·21	0·25	1·28	15·04	100·02	2·441
III.	43·18	39·21	0·15	trace	0·08	3·39	14·23	100·24	2·460

Analysis III is of a similar clay from Grubb mines, near Roanoke, Virginia.

L. J. S.

The Sodium Potassium Nephelites. N. L. Bowen (*Amer. J. Sci.*, 1917, [iv], **43**, 115—132).—The results are given of an experimental investigation of the binary system $NaAlSiO_4$–$KAlSiO_4$. The sodium compound occurs in two enantiomorphous forms, nephelite and carnegeite, with an inversion point at 1248°. The higher temperature form, carnegeite, melts at 1526°. The potassium compound also shows two forms: kaliophilite, isomorphous with nephelite, and an orthorhombic form with twinning, like that of aragonite. The orthorhombic form is apparently stable at temperatures above 1540° and melts at about 1800°. The potassium compound has a eutectic with carnegeite at 1404°. With nephelite it forms an unbroken series of solid solutions. It is concluded, therefore, that $NaAlSiO_4$ and $KAlSiO_4$ are the fundamental molecules of natural nephelite. The presence of calcium and of excess of silica in the natural mineral is explained by the solid solution of the albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) molecules (compare A., 1912, ii, 176, 774). L. J. S.

An Application of Polydimensional Geometry to Chemico-mineralogical Problems. The Composition of Tourmaline. H. E. Boeke (*Jahrb. Min.*, 1916, ii, 109—148).—For the quantitative graphical representation of systems of more than four components the author advocates the use of geometrical conceptions in four or more dimensions. The simpler properties of four-dimensional space are considered in some detail, and the method is then applied to a study of the composition of tourmaline.

The theories which have been advanced to explain the composition of the tourmalines fall into two groups: (1) those which postulate two or three distinct molecules, which, mixed in suitable proportions, will form any of the known varieties of tourmaline; (2) those which start from one or more fundamental forms in which replacement of certain chemical elements or groups in equivalent proportions can take place. After a critical examination of old analyses and of fifty-four new trustworthy analyses of tourmalines the author comes to the following conclusions: The relative amounts of silica and boric acid show a constant ratio, $SiO_2 : B_2O_3 = 4 : 1$. If the mono-, bi-, and ter-valent metals be replaced by hydrogen equivalents, the ratio total hydrogen : Si varies between 56 : 12 and 72 : 12, but is generally 20 : 4. It appears to be very probable that the general formula $H_{20}Si_4B_2O_{21}$ first suggested by Penfield and Foote, is correct.

For the graphic representation of tourmaline the author distinguishes five components: *a*, H_2O; *b*, R_2O ($=Na_2O+Li_2O+K_2O$); *c*, RO ($=MgO+CaO+FeO+MnO$); *d*, R_2O_3 ($=Al_2O_3+Fe_2O_3+Ti_2O_3$); *e*, $SiO_2+B_2O_3$.

From an origin *E*, representing the constant component ($SiO_2+B_2O_3$), four axes all at right angles to one another are drawn, each of length = 100, ending in the points *A*, *B*, *C*, *D*, representing the pure components H_2O, R_2O, RO, and R_2O_3. The five points *A* to *E* describe a four-dimensional pentahedron, rectangular at *E*, bounded by ten edges, ten planes, and five three-dimensional spaces. The composition of any tourmaline is represented by a point within this pentahedron. For the examination of the mutual relationships of the four variable components in pairs, six plane projections are necessary. It is found that the points representing the composition of tourmaline in four-dimensional space S_4 do not belong to one three-dimensional space S_3, nor to a single plane S_2. If the formula of Penfield and Foote were strictly correct, all tourmaline points should fall within one tetrahedron in S_3. It remains to be seen whether the departures from the formula $H_{20}Si_4B_2O_{21}$ are to be attributed to analytical errors or to the incorrectness of the formula. E. H. R.

Analytical Chemistry.

Graph for Correcting Volumes of Gases to 0° and 700 mm. MARCEL RIGOTARD (*Ann. Chim. anal.*, 1917, **22**, 21—23).—The graph is constructed from the correction factors given in the following table:

	710 mm.	720 mm.	730 mm.	740 mm.	750 mm.	760 mm.	770 mm.
10°......	0·9013	0·9138	0·9266	0·9393	0·9519	0·9647	0·9775
15°......	0·8857	0·8981	0·9105	0·9230	0·9354	0·9480	0·9605
20°......	0·8706	0·8828	0·8950	0·9073	0·9195	0·9318	0·9441
25°......	0·8560	0·8680	0·8801	0·8922	0·9042	0·9162	0·9283

For example, the volume of a gas measured at 20°/740 mm. is multiplied by 0·9073 to obtain its volume at 0°/760 mm.
W. P. S.

Urotropine [Hexamethylenetetramine] as a Microchemical Reagent. R. VIVARIO and M. WAGENAAR (*Pharm. Weekblad*, 1917, **54**, 157—161).—A description of crystalline derivatives formed by urotropine with metallic salts, with a summary of the literature. A. J. W.

Lunge's Method for the Rapid Estimation of Sulphur in Roasted Ores. J. B. PÉRÉGRIN (*Ann. Chim. anal.*, 1917, **22**, 26—27).—A quantity of 3·2 grams of the powdered substance is mixed with 2 grams of sodium hydrogen carbonate and heated gently for ten minutes, then for twenty minutes at a dull red heat. After cooling, the mixture is treated with water, boiled, the solution filtered, the insoluble portion washed with boiling water, and the filtrate titrated with *N*/1-hydrochloric acid. Two grams of sodium hydrogen carbonate are also titrated under similar conditions; the difference in the quantities of hydrochloric acid used for the two titrations is divided by 2 to obtain the percentage quantity of sulphur in the sample. The results obtained by the method are sufficiently trustworthy for practical purposes. W. P. S.

Benedict's Method for the Estimation of Total Sulphur in Urine. MAURICE H. GIVENS (*J. Biol. Chem.*, 1917, **29**, 15—17. Compare Benedict, A., 1909, ii, 827; 1911, ii, 330).—The decrepitation which sometimes occurs during the oxidation of the sulphur compounds with copper nitrate is avoided if the urine is mixed with the Benedict reagent and slowly evaporated to dryness over a hot plate. The residue is then directly ignited over a Bunsen burner. H. W. B.

Lunge's Method for the Rapid Estimation of Arsenic in Sulphuric Acid. J. B. PÉRÉGRIN (*Ann. Chim. anal.*, 1917, **22**, 24—25).—This method was found to be trustworthy; the results tend to be slightly too low, but a correcting factor may be found and applied in practice. Twenty c.c. of the sulphuric acid are diluted to about 50 c.c. and treated for ten minutes with a current of sulphur dioxide; the mixture is then heated, and a current of carbon dioxide is passed through it until all sulphur dioxide has been expelled. After further dilution, the solution is neutralised with sodium hydrogen carbonate and titrated with $N/20$-iodine solution. W. P. S.

A Colloido-chemical Phenomenon as Indicator in Quantitative Analysis. J. F. SACHER (*Koll. Zeitsch.*, 1916, **19**, 276—277).—In the estimation of lead by titration with a solution of ammonium molybdate, the supernatant liquid is turbid so long as the reaction is incomplete, but this turbidity disappears suddenly at the end-point. The turbidity is due to colloidal lead molybdate, and the coagulation of this serves to indicate the end-point.

In practice, the solution of lead, acidified with acetic acid, is heated at 70—80°, and the progress of the titration is determined by removing a drop of the solution and observing its optical condition. The end-point is independent of the quantity of acetic acid present, and the method is to be preferred to the older procedure in which tannin is used as indicator. H. M. D.

[Estimation of Copper in Blood of Molluscs and Crustacea.] CH. DHÉRÉ (*J. Physiol. Path.-gen.*, 1916, **16**, 985—997).—See this vol., i, 236.

Estimation of Manganese in High-speed Steels. C. T. NESBITT (*Chem. News*, 1917, **115**, 61—62).—On account of the difficulty of obtaining bromine, methods of analysis which do not require the use of bromine are to be preferred for high-speed steels. In the basic acetate method, bromine may be replaced by ammonium persulphate when that salt is obtainable in a pure state, but with most of the persulphate now supplied the results are always high. Potassium chlorate and hydrochloric acid are not satisfactory. Hydrogen peroxide or sodium peroxide also yields a precipitate which readily redissolves if any large excess of ammonium salts is present. The zinc oxide and cadmium carbonate methods give lower results than the standard gravimetric method.

Oxidation with bismuthate is to be preferred, and the following procedure must be adopted for high-speed steels. 1·1 Grams of steel drillings are dissolved in 12 c.c. of concentrated hydrochloric acid and evaporated to a syrup with 5 c.c. of concentrated nitric acid. After adding exactly 7 c.c. of concentrated sulphuric acid and rinsing down with water, the mixture is heated strongly for fifteen minutes, cooled, mixed with 30 c.c. of nitric acid (D 1·2) and 20 c.c. of water, boiled, and filtered through pulp. The precipitated tungstic oxide is washed, and the filtrate and washings are mixed with 15 c.c. of nitric acid to bring up the strength to D 1·2, boiled, oxidised with a little bismuthate, and cleared with 10 c.c. of sulphurous acid. After boiling off sulphur dioxide, the liquid is cooled, oxidised with 0·2 gram of bismuthate, shaken for two or three minutes, and filtered through asbestos. The residue is washed with 3% nitric acid, and titrated with ferrous sulphate and potassium permanganate. There is a transient pink coloration shortly before the true end-point. The heating to strong fuming with sulphuric acid and addition of sulphurous acid are necessary to remove chromium. Solution in hydrochloric acid and subsequent addition of sulphuric acid is much more rapid than direct solution in sulphuric acid. C. H. D.

Estimation of Tungsten and Silicon in Tungsten Steel. C. F. van Duin (*Chem. Weekblad*, 1917, **14**, 169—173).—The author finds that Ziegler's method for the estimation of tungsten in tungsten steel is untrustworthy, and that Zinberg's method gives inaccurate results for tungsten and too high results for silicon.

A. J. W.

Analysis of Babbit Metal and Alloys of Tin, Antimony, Lead, and Copper. E. W. Hagmaier (*Met. & Chem. Eng.*, 1917, **16**, 84—85; from *J. Soc. Chem. Ind.*, 1917, **36**, 221).—The following process is recommended: *Antimony*.—1 Gram of filings is heated with water (10 c.c.) and sulphuric acid (25 c.c.) until no black particles remain. The cooled solution is diluted with water (100 c.c.) and hydrochloric acid (10 c.c.), boiled for ten minutes to expel sulphurous fumes, and titrated with potassium permanganate after being cooled and further diluted with water (100 c.c.). *Tin*.—The sample (0·5 gram) is dissolved in hydrochloric acid (with potassium chlorate if necessary), and the tin estimated by titration with *N*/10-iodine solution after reduction with soft iron and hydrochloric acid. *Lead*.—Solution is effected by dilute nitric acid in the presence of a large excess of tartaric acid. Sulphuric acid is then added, and the solution boiled sufficiently to expel all nitrous fumes, but without charring the tartaric acid; the lead sulphate is subsequently collected, dissolved in ammonium acetate solution, and the lead reprecipitated and weighed as chromate. *Copper*.—Solution is effected as in the preceding case, and the filtrate from the lead sulphate is further acidified with hydrochloric acid and heated with pure aluminium. The precipitated copper is collected and redissolved in dilute nitric acid for determination by the electrolytic or iodide method. H. W.

Biochemical Reactions for Distinguishing between the Three Isomeric Dihydroxybenzenes: Catechol, Quinol, and Resorcinol. JULES WOLFF (*Compt. rend. Soc. Biol.*, 1916; from *J. Pharm. Chim.*, 1917, [vii], **15**, 94).—An intense blue coloration is obtained when 2 c.c. of a 0·1% catechol solution are treated with 2 drops of a glycerol extract of *Russula delica* (or other fungus rich in laccase), 5 drops of 3% potassium iodide solution containing 2% of soluble starch, and 3 drops of 5% acetic acid. The reaction is not given by quinol, but in this case a blue coloration develops gradually when *N*/1-sulphuric acid is used in place of the acetic acid. Resorcinol does not give a coloration either in the presence of acetic acid or of sulphuric acid. W. P. S.

A New Reaction for the Water-soluble, Active Glucoside from Digitalis Leaves. F. WRATSCHKO (*Zeitsch. allg. Österr., Apoth.-Ver.*, 1916, **54**, 263; from *Chem. Zentr.*, 1916, ii, 849).—A few c.c. of orcinol–hydrochloric acid reagent (0·2 gram of orcinol, 100 c.c. of concentrated hydrochloric acid, 4 drops of ferric chloride, solution) are heated to boiling, a few drops of the liquid under investigation are added, and the mixture is shaken. A green to blue colour develops, or, at greater concentration, a dark precipitate is formed. The solution is treated with an equal volume of water and shaken with amyl alcohol, whereby the latter is coloured green to dark blue; in the course of a few hours, this colour changes to a more stable lilac to carmine-red tint. The intensity of the colour is dependent on the digoside content of the liquid under investigation. The reaction is very sensitive. In the rare case in which the presence of free pentoses is considered possible, a preliminary extraction of the active glucoside with chloroform is necessary; the chloroform is removed, the residue dissolved in alcohol, and the solution tested as described. *Strophanthus* tincture and the aqueous and chloroform extracts of *Strophanthus* seeds also show this reaction. H. W.

Detection of Hydrocyanic Acid. GEORGE W. ANDERSON (*J. Soc. Chem. Ind.*, 1917, **36**, 195—196).—The sensitiveness of various methods for the detection of hydrocyanic acid has been investigated. For this purpose, solutions of potassium cyanide (98·5%) were prepared ranging in strength from 0·00001% to 0·1%, and therefore containing 0·00000393 to 0·0393 gram of cyanogen in 100 c.c. For each test, 10 c.c. of solution were employed, and all the reagents were examined and found to be pure.

Detection of hydrocyanic acid as silver cyanide.—A precipitate of silver cyanide is formed when silver nitrate is added to a solution of hydrocyanic acid or an alkali cyanide in presence of nitric acid when the dilution does not exceed 0·00039 gram of cyanogen per 10 c.c. In more dilute solution an opalescence is produced. The limit of sensitiveness is reached in a 0·0001% solution. Supersaturation of the solution with ammonia before addition of silver nitrate and nitric acid does not lead to better results. Excess of acid must be avoided, but excess of silver nitrate is necessary. *Detection as Prussian-blue.*—The reaction was found to fail at concentrations lower than 0·001%; at this concentration, the coloration only appeared after half to one hour. This result is due to incomplete conversion of cyanide into ferrocyanide, since the presence of the latter can be detected at dilutions corresponding with 0·000024 gram of cyanogen. *Detection as thiocyanate.*—The tests were carried out according to the directions of Link and Möckel, and showed that when 0·00039 gram of cyanogen (0·01%) or more is present in 10 c.c., a deep red colour appeared, which became lighter with increasing dilution, finally showing a faint orange tint. The limit of sensitiveness is reached with a 0·0001% solution (0·0000039 gram of cyanogen per 10 c.c.). *Detection by means of picric acid.*—A series of tests showed the sensitiveness of this reaction to be limited, and, moreover, the same coloration may be produced by impurities in the acid or alkali or by reducing substances (sugar, sulphur dioxide, etc.). *Detection by means of guaiacol.*—This test, known as the Schönbein-Pagenstecher reaction, is the most sensitive for the detection of hydrocyanic acid. Adopting the modification suggested by Maisel, the author has been able to detect as little as 0·00000039 gram of cyanogen in 10 c.c. (0·00001% potassium cyanide). The reaction, however, is easily disturbed by the presence of alien substances, such as ammonia or cigar smoke.

The author draws the conclusion that, although the Schönbein-Pagenstecher method is the most sensitive, it can only be used as a preliminary test in conjunction with use of the other reactions, for example, the Prussian-blue or silver cyanide test, of which the latter is often preferred in forensic chemistry. This test, however, generally requires a double distillation of the original solution under examination in order to obtain a distillate free from chlorine. The Prussian-blue test will suffice for ordinary purposes, whilst the thiocyanate reaction may be useful in special cases. The picric acid reaction cannot be recommended. H. W.

Estimation of Hydrocyanic Acid in Sorghum vulgare. J. J. Willaman (*J. Biol. Chem.*, 1917, **29**, 25—36).—See this vol., i, 245.

Estimation of Unsaponifiable Matter in Oils and Fats. J. Davidsohn (*Chemische Umschau Fett. Harz-Ind.*, 1916, **23**, 130—131; from *Chem. Zentr.*, 1916, ii, 1076).—Five grams of fat are saponified with *N*/2-alcoholic potassium hydroxide (50 c.c.), and the solution is evaporated nearly to dryness. The residue is dissolved in water and twice extracted with ether. The ethereal solution is distilled and evaporated to dryness after addition of a little alcohol. The residue is weighed, warmed with water (50 c.c.), and titrated with *N*/10-acid in the presence of methyl-orange. The weight of soap thus found is deducted from that of the extract. H. W.

Method for Accurately Estimating Arginine in Proteins. B. C. P. JANSEN (*Chem. Weekblad*, 1917, **14**, 125—129).—Arginine can be estimated quantitatively in proteins by the action of arginase and urease on the hydrolysed product after elimination of the ammonia. The arginase decomposes the arginine, with formation of an equimolecular proportion of urea, which is converted by the urease into ammonium carbonate. A. J. W.

Factors Involving the Accuracy of Creatinine Estimations in Human Blood. ALEXANDER O. GETTLER [with RUTH OPPENHEIMER] (*J. Biol. Chem.*, 1917, **29**, 47—56. Compare Folin and Doisy, this vol., ii, 159).—The authors point out that oxalates have a strong bleaching action on the picramic acid colour, and therefore only the requisite amount of oxalate should be used to prevent the coagulation of the sample of blood. The colour produced by picric acid and creatinine in the presence of alkali is only due in part to the creatinine, and it is therefore inaccurate to reckon the total colour produced as due to this substance. The authors give a table, from which the actual amount of creatinine can be determined from any intensity of colour produced under standard conditions.

The amount of creatinine in normal blood ranges from 0·1 to 0·4 mg. in 100 c.c. The values of 1 to 2 mg. in 100 c.c. given by Folin and Denis (A., 1914, i, 764) are much too high. H. W. B.

Tests for certain Narcotic and Anæsthetic Drugs. E. H. HANKIN (*Indian J. Med. Research*, 1916, **4**, 237—255).—Colour reactions of a large number of alkaloids, narcotic substances, etc., are recorded, and more particularly those given by cycloform, β-eucaine, orthoform, nirvanine, anæsthesine, novocaine, holocaine, acoine, stovaine, and alypine. Nitric acid gives a yellow coloration with cycloform, reddish-brown with holocaine, and brownish-black with acoine. Alypine, cocaine, tropacocaine, and α-eucaine yield red crystals when their solutions are mixed with alum solution and the mixtures added to potassium permanganate crystals on a microscope slide; β-eucaine and stovaine form red, oily drops with this reagent. Most of the substances give a white precipitate when treated with Fehling's solution. Reactions with sulphuric acid and potassium iodate, sulphuric acid and hexamethylenetetramine, and with bromine are also described. W. P. S.

General and Physical Chemistry.

The Refractive Power and the Specific Refraction of Dispersoids. George Wiegner (*Kolloid Zeitsch.*, 1917, **20**, 7—19).—A theoretical discussion of the various formulæ which have been suggested as affording a measure of the refractive power of a liquid. The refractivity R of the disperse phase in colloidal solutions of arsenious sulphide, ferric hydroxide, tannin, and silicic acid is calculated from the refractive indices and densities of solutions of variable concentration on the assumption that $R = n - 1/d$ or $= n^2 - 1/(n^2 + 2)d$, and that the mixture rule is applicable to the refractivity of the colloidal system. The ordinary mixture formula involving R is transformed so as to express the refractive index and specific volume of the colloidal system in terms of the corresponding quantities for the disperse phase and the dispersive medium.

H. M. D.

The Periodic System of the Elements and Spectrum Analysis. Viktor Kutter (*Physikal. Zeitsch.*, 1917, **18**, 16—17). —The metallic elements may be roughly divided into four groups according to the facility with which their spectra may be obtained. The elements of the first group give a satisfactory spectrum in the Bunsen flame. In the case of elements belonging to the second group the flame spectrum is only feebly developed, but spark discharge gives a good spectrum. The elements of the third and fourth groups give no spectrum in the Bunsen flame, but are distinguished by the fact that elements in the third group yield a spectrum with ordinary spark discharge, whilst those in the fourth group require condensed spark discharge.

The grouping of the elements on this basis gives some indication of their relative volatilities, and attention is directed to the circumstance that this volatility appears to be a periodic function of the atomic weight. H. M. D.

The Arc Spectrum of Samarium. Josef Maria Eder (*Sitzungsber. K. Akad. Wiss. Wien*, II., A., **125**; from *Chem. Zentr.*, 1917, i, 55. Compare this vol., ii, 1).—The variations in the wave-length tables of samarium when different specimens are used make it appear doubtful if the substance remains uniform after fractional separation from europium. Re-examination of 1046 lines of the arc spectrum shows samarium to be a spectroscopically well-characterised element which may contain small amounts of a possibly new, unknown element. Samarium itself is probably the neighbouring element to europium in the periodic system. With small dispersion the samarium spectrum appears to consist of strong lines which, at greater dispersion, are found to be resolved into very many lines of similar brightness. H. W.

Solvent Effect and Beer's Law. ALFRED WALTER STEWART and ROBERT WRIGHT (T., 1917, **111**, 183—187).—Previous observations on the absorption spectra of aqueous and ethyl-alcoholic solutions of iodine (A., 1911, ii, 1043) have shown that Beer's law does not represent the variation of the absorption with the concentration in either of these solvents. In aqueous solution the absorption increases with the concentration, whereas the converse holds for alcoholic solutions.

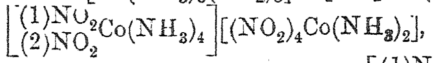
Further experiments with iodine in other solvents show that the absorption increases with concentration in chloroform and carbon tetrachloride, but decreases with increasing concentration in ethyl ether and methyl acetate. Light petroleum resembles the oxygenated solvents, but its influence is only slight. It is suggested that the presence of oxygen in the solvent is mainly responsible for the observed differences. H. M. D.

The Absorption Spectrum of Nitric Acid Vapour. KONR. SCHAEFER [with ST. DEICHSEL) (*Zeitsch. anorg. Chem.*, 1916, **98**, 70—76. Compare this vol., ii, 61).—On account of the rapid decomposition of nitric acid vapour by light, it is necessary to maintain a stream of the vapour through the absorption tube during the photographing of the spectrum. The absorption tube is electrically heated at 130°, the constant boiling acid being used. There is no absorption band, the curve being very similar to that given by a liquid 98·7% acid. The NO_3 group in the vapour is therefore in a similar state to that in the alkyl nitrates and in the concentrated acid. C. H. D.

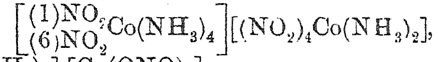
Optical Investigation of Mixtures of Nitric and Sulphuric Acids. KONR. SCHAEFER [with H. NIGGEMANN] (*Zeitsch. anorg. Chem.*, 1916, **98**, 77—85. Compare this vol., ii, 61).—Pure 95% sulphuric acid is optically transparent, but the addition of sulphur trioxide to bring up the strength to 100% causes absorption. The trioxide is rendered optically clear by redistillation. The two acids are mixed in a modified Beckmann apparatus, but the heat developed is liable to cause decomposition of the nitric acid, so that it is better to add finely powdered potassium nitrate to the sulphuric acid. The absorption limit of 0·2*N*-nitric acid is displaced towards the ultra-violet even by 20% sulphuric acid, the absorption curve being flattened at the same time, and this effect increases with increasing concentration of sulphuric acid. The acid is considered to act as a dehydrating agent, displacing the equilibrium between the two modifications of the NO_3 group. C. H. D.

Researches on the Absorption Spectra of Metal Ammines. II. (A.) Absorption Spectra and Electrolytic Conductivity of Aqueous Solutions of Co-ordination Polymeric Nitroammine-cobalt Complexes. (B.) Absorption Spectra of Aqueous Solutions of Polynuclear Ammine-cobalt Complexes. YUJI SHIBATA [with K. MATSUNO] (*J. Coll. Sci. Tokyo*, 1916, **37**, 1—31).—(*A*.) In a previous paper (A., 1916, ii, 277), the absorption spectra of complex cobaltammines have been studied, the complex anions or cations being combined with the ordinary inorganic and simple cations or anions. The investigation has now been extended to the case of salts where both the anions and cations are complex, the salts investigated being the following co-ordination polymerides of the general formula

$$n[\mathrm{Co(NH_3)_3(NO_2)_3}]:\ [\mathrm{NO_2{\cdot}Co(NH_3)_5}][\mathrm{(NO_2)_4Co(NH_3)_2}]_2,$$

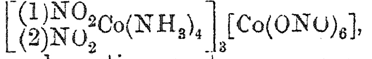


$$\left[\begin{matrix}\mathrm{(1)NO_2}\\\mathrm{(2)NO_2}\end{matrix}\mathrm{Co(NH_3)_4}\right][\mathrm{(NO_2)_4Co(NH_3)_2}],$$

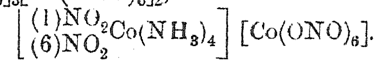


$$\left[\begin{matrix}\mathrm{(1)NO_2}\\\mathrm{(6)NO_2}\end{matrix}\mathrm{Co(NH_3)_4}\right][\mathrm{(NO_2)_4Co(NH_3)_2}],$$

$$[\mathrm{NO_2{\cdot}Co(NH_3)_5}]_3[\mathrm{Co(ONO)_6}]_2,$$



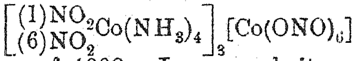
$$\left[\begin{matrix}\mathrm{(1)NO_2}\\\mathrm{(2)NO_2}\end{matrix}\mathrm{Co(NH_3)_4}\right]_3[\mathrm{Co(ONO)_6}],$$



$$\left[\begin{matrix}\mathrm{(1)NO_2}\\\mathrm{(6)NO_2}\end{matrix}\mathrm{Co(NH_3)_4}\right][\mathrm{Co(ONO)_6}].$$

The absorption spectra were examined in solutions varying in concentration from 1/100 to 1/10,000 equivalent. All the solutions were stable, and the absorption conformed to Beer's law.

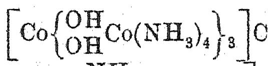
The absorption spectra show that the above six salts can be divided into two classes, the first class comprising the first three salts and the second class the last three salts. The salts in the first class all show a characteristic absorption band (in the strict sense of the word it is not a band, since there is no maximum point of absorption) at a frequency of 2200, and two other absorption bands at frequencies of 3000 and 4000. The second band, frequency 3000, is common to all the nitro-ammine–cobalt complexes. The salts in the second class have two or three absorption bands, the first being at a frequency of 2100, the second at 3000, and the third, which exists in the case of



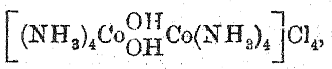
$$\left[\begin{matrix}\mathrm{(1)NO_2}\\\mathrm{(6)NO_2}\end{matrix}\mathrm{Co(NH_3)_4}\right]_3[\mathrm{Co(ONO)_6}]$$

only, at a frequency of 4000. In general, it may be said that the absorption spectra of the above six polymerides containing complex anions and cations are additive, except in the case of the characteristic band peculiar to the first three. Investigation of the electrolytic conductivity of these salts showed, by comparison with the conductivities of complex salts with either the anion or cation of a simple character, that it was normal in every case. The characteristic absorption band is explained, in the light of Stark's theories, by the presence of a "loosened" valency electron in the first three salts.

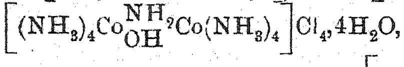
(*B*.) The absorption spectra of the following polynuclear complexes have been studied:



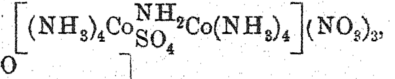
$$\left[\mathrm{Co}\left\{\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}\mathrm{Co(NH_3)_4}\right\}_3\right]\mathrm{Cl_6},$$



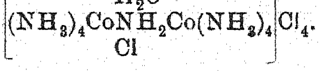
$$\left[\mathrm{(NH_3)_4Co}\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}\mathrm{Co(NH_3)_4}\right]\mathrm{Cl_4},$$



$$\left[\mathrm{(NH_3)_4Co}\begin{matrix}\mathrm{NH_2}\\\mathrm{OH}\end{matrix}\mathrm{Co(NH_3)_4}\right]\mathrm{Cl_4,4H_2O},$$



$$\left[\mathrm{(NH_3)_4Co}\begin{matrix}\mathrm{NH_2}\\\mathrm{SO_4}\end{matrix}\mathrm{Co(NH_3)_4}\right]\mathrm{(NO_3)_3},$$



$$\left[\mathrm{(NH_3)_4Co}\underset{\mathrm{Cl}}{\overset{\mathrm{H_2O}}{\mathrm{NH_2}}}\mathrm{Co(NH_3)_4}\right]\mathrm{Cl_4}.$$

The dilutions varied from $N/100$ to $N/10,000$, except with the fourth salt, where they varied from $N/400$ to $N/4000$. Satisfactory results could not be obtained from the pure aqueous solutions, owing to gradual hydrolysis with the separation of cobalt hydroxide. The acid solutions, acidified with the corresponding mineral acid, were stable and conformed to Beer's law.

Each of the salts gave, in acid solution, practically the same absorption spectra, showing two absorption bands at frequencies of approximately 2000 and 3400—3500 respectively. This is ascribed to the fact that the cobalt complexes in the above salts, if one neglects the bridged linkings, are the same. The bridged linkings are very weak, as shown by the ready hydrolysis of the salts, and have no effect on the absorption of light. T. S. P.

Absorption of the Ultra-violet Rays by some Chloro-derivatives of Ethane, Ethylene, and Acetylene. G. MASSOL and A. FAUCON (*Compt. rend.*, 1917, **164**, 308—310).—An examination of the ultra-violet absorption spectra of hexachloroethane, tetrachloroethylene, *s*-tetrachloroethane, and acetylene in alcoholic solution. Hexachloroethane and *s*-tetrachloroethane have practically the same transparency for the ultra-violet rays. Tetrachloroethylene is much less transparent than these, and this is attributed to the fact that it is an unsaturated compound. None of these compounds shows the broad band characteristic of chlorine, the absorption being, in all cases, unilateral. Neither of the unsaturated compounds tetrachloroethylene or acetylene gives any special band. The limits of transmission of the ultra-violet rays by alcoholic solutions of the above compounds, of varying thickness, are tabulated. W. G.

Spectrochemistry of Benzene Derivatives and Cinnamic Esters. K. VON AUWERS (*Annalen*, 1917, **413**, 253—309).—See this vol., i, 266.

The Rotatory Power of Liquid Crystals. PAUL GAUBERT (*Compt. rend.*, 1917, **164**, 405—406. Compare Vorländer and Huth, A., 1911, ii, 165).—The author has used a new method for the measurement of the rotatory power of liquid crystals by superimposing on such a preparation a substance having a rotatory power, and determining in monochromatic light the displacement of the arms of the black cross obtained with Nicol prisms. The rotatory power, which is at first low, increases as the wave-length of the reflected colour increases. For each kind of rays, the substance is at first lævorotatory and then dextrorotatory. In some cases this change, in sense of the rotation, occurs just at the moment when the preparation reflects the rays. At this phase, one of the two circular rays is absorbed, and there is, consequently, no rotatory power for the colour considered, but when the tint passes towards the red, the rotatory power reappears in the inverse sense and goes on increasing. W. G.

The Action of Penetrating Radium Rays on Colloids. II. ALBERT FERNAU and WOLFGANG PAULI (*Kolloid Zeitsch.*, 1917, **20**, 20—33. Compare A., 1915, ii, 722).—In the further investigation of the action of penetrating radiation on inorganic colloids, experiments have been made with colloidal solutions of ceric hydroxide prepared by dialysis of a solution of ceric ammonium nitrate.

These colloidal solutions change in a marked manner with time, the ageing being accompanied by a diminution in viscosity, a gradual loss of the faculty to gelatinise, and by a diminution in the sensitiveness towards electrolytes. The change is irreversible, and is accelerated by rise of temperature. It is supposed that the ageing is due to the gradual dehydration of the sol particles.

The ageing of ceric hydroxide sols is very largely modified under the influence of β- or γ-rays from radium. The first effect consists in an accelerated rate of diminution of the viscosity, but this effect is succeeded by a second, in which the viscosity of the sol increases to a value very large in comparison with that of the freshly dialysed sol. The progress of the second stage is not dependent on the continued exposure of the sol to the action of the active rays, for if the exposure is made intermittent, it is found that the course of the viscosity–time curve is quite unchanged. A further curious effect is observed when the source of the radiation is removed before the end of the first stage in the ageing process. In these circumstances, the second stage in the ageing process sets in, and the viscosity of the sol increases very considerably, attains a maximum value, and subsequently decreases almost as rapidly as it increased before the attainment of the maximum. The jelly obtained when the radiation is allowed to act sufficiently long appears to be perfectly stable.

Similar changes in the viscosity are produced by the addition of electrolytes, although the effects are readily distinguishable. On the addition of a quantity of an electrolyte, which is not sufficient to produce coagulation, there is an immediate drop in the viscosity of the sol, and this is then succeeded by a gradual increase in the viscosity, the final result being a solid jelly. If the quantity of added electrolyte is smaller, the initial diminution in the viscosity is followed by an increase to a maximum, and thereafter the viscosity sinks slowly. The viscosity–time curve is thus very similar to that which represents the changes occurring after the ceric hydroxide sol has been exposed for a short time to the action of β- or γ-rays. There is, however, a marked difference between the two, in that the rising and falling branches on opposite sides of the maximum are much steeper in the case where the sol has been under the influence of the radiation. A further difference is found in the fact that the jelly produced by the action of electrolytes is unstable. It gradually becomes turbid, contracts, and sets free water.

Electrometric measurements of the chlorine ion concentration in sols to which sodium chloride has been added show that chlorine ions disappear at once when the electrolyte is added to the sol, but that no further change occurs during the second stage of the ageing process.

Although, in a general way, the ageing of sols is supposed to be due to the gradual formation of larger colloidal particles by a process of aggregation, it is probable that the effects described by the authors are connected with changes in the degree of hydration. It is probable that ceric hydroxide and other metallic hydroxide sols are highly hydrated, and in this way differ from hydrophobic colloids, such as the metallic and the sulphide sols. Under the influence of electrolytes or β- or γ-rays, the electrical charge of the colloidal particles is neutralised, and this is accompanied by a diminution in the degree of hydration, and results in a lowering of the viscosity, gradual when the sol is subjected to β- or γ-rays and immediate when an electrolyte is added. The increase in viscosity in the second stage of the ageing process is then due to the aggregation of the electrically neutral particles, a process which takes place with a velocity comparable with that of crystallisation and similar processes.

The attainment of a maximum viscosity and the subsequent fall which is observed when the added electrolyte is very small in quantity or the time of exposure to the rays is comparatively brief is more difficult to explain, and the suggestion is put forward that this peptonisation is due to the action of electrically charged colloid particles which are enclosed by the jelly resulting from the aggregation of the electrically neutral particles. In support of this view, it has been found that ceric hydroxide jelly may be readily peptonised by the addition of the corresponding sol.

H. M. D.

Some Particular Cases of Current-potential Lines. II. A. H. W. Aten (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 768—778).—The considerations put forward in the previous paper (this vol., ii, 163) are applied to the electrolysis of solutions containing halogen ions with a silver anode. The most favourable conditions for the separation of halogen in the form of silver haloid at the anode with a minimum loss of silver by anodic dissolution are shown to be deducible from the theory put forward, and these conditions are for the most part those which have been found most satisfactory according to the empirical experiments which have been made by various observers. The fact that the accuracy with which the halogens can be estimated by this method increases with increase in the atomic weight of the halogen is due to the diminishing value of the ionic solubility product of the corresponding silver haloids.

The conditions favourable to the formation of insoluble metallic compounds by the anodic dissolution of the metal are also derived and found to agree with those indicated by practice.

The author's views are also applied to the electrolysis of solutions of complex salts, the alkali silver cyanide solution being specially considered, and it is shown that the conditions under which silver cyanide is deposited on the anode, thereby increasing the resistance and reducing the current, may be deduced from the theory. To avoid this in practice, the current density must not exceed a certain value, which, of course, depends to some extent on the concentration of the solution. H. M. D.

The Surface Electric Double-layer of Solid and Liquid Bodies. J. FRENKEL (*Phil. Mag.*, 1917, [vi], **33**, 297—322).—A theoretical paper in which the origin of the electrical double-layer at the surface of solids and liquids is discussed.

It is assumed that the atoms consist of positive nuclei with electrons rotating about them, and by considering the surface layer it is shown that this atomic model necessarily gives rise to an electric double-layer, with the negative electrification external to the positive in the case of all metallic substances.

The phenomena associated with the existence of this double-layer are examined, and it is shown that the intrinsic potentials of all metals are positive and of the same order of magnitude as the corresponding ionising potentials. The intrinsic potentials tend to increase with the valency of the metals. In the case of insulators, the intrinsic potential may be positive or negative, such substances being distinguished from conductors by the absence of free electrons. Contact electromotive forces, whether of metals or dielectrics, are shown to be due to differences in the intrinsic potentials.

The electric double-layer is supposed to afford an explanation of the phenomena of surface tension. On the assumption that the surface tension depends exclusively on the energy of the electric double-layer and not at all on cohesive forces, the author calculates the atomic radii and the intrinsic potentials for a number of metals. The values thus obtained vary from two to six volts and correspond more or less with the ordinary electrochemical series. In the case of the atomic radii, the values are approximately equal to those corresponding, on Bohr's theory, with stationary orbits of the second order.

The theory affords an explanation of the relatively low surface tension of non-conductors compared with that of the metals, and also of the state of stress which is usually defined in terms of the internal pressure. H. M. D.

The Effect of Rust on the Corrosion of Iron and Steel. JAMES ASTON (*Trans. Amer. Electrochem. Soc.*, 1916, **29**, 449—464).—Measurements of the current in cells containing tap water through which air is bubbled show the influence of rust in accelerating the further rusting of iron and steel. Wet rust is anodic to bare iron, whilst dry rust is cathodic. The current densities are comparable with those given by the couples iron–carbon or iron–copper. When both electrodes are coated with rust of similar character, there are always sufficient differences to cause a flow of current. Wet ferric hydroxide has a high resistance. The anodic effect produced by wet rust is also caused by other colloidal hydroxides, gelatin, gum, parchment, and filter paper, the action being probably one of preventing access of oxygen. Ferroxyl tests confirm the results of current measurements. Dry rust behaves like fresh wet rust if immersed for a sufficient time in water. C. H. D.

The Theoretical Existence of a Second Critical Point. Maurice Prud'homme (*J. Chim. phys.*, 1916, **14**, 445—448).—Analysis of the van der Waals's equation leads the author to the conclusion that a second critical point is theoretically possible. The characteristics of this point are subjected to analysis. H. M. D.

Determination of Melting Points at Low Temperatures. Alfred Stock (*Ber.*, 1917, **50**, 156—158).—Two forms of a device are described by means of which the difficulty of determining a melting point with a non-transparent bath is overcome. It is therefore equally serviceable for low and high temperatures. It consists essentially of a thin-walled tube about 6 mm. wide and a glass rod about 2 mm. thick, elongated to act as a pointer. By suitable means a ring of the solid substance is deposited on the wall of the tube a short distance from the sealed end and the glass rod is rested on it. The melting point is taken when the upper end of the pointer is observed to sink. J. C. W.

The Tension of Saturated Vapour at Low Temperatures and the Chemical Constant. E. Ariès (*Compt. rend.*, 1917, **164**, 477—480. Compare *ibid.*, 1917, **164**, 343).—A mathematical paper, in which the author deduces for the value of the chemical constant $A=(Ke/R)^{m-1}$, where m is the ratio C/c of the two specific heats of perfect gases. W. G.

Computation and Measurement of the Complex Molecules of Certain Vapours according to the New Condensation Theory. L. Andrén (*Ann. Physik*, 1917, [iv], **52**, 1—71).—The condensation of water, ethyl alcohol, and benzene vapour in admixture with air, carbon dioxide, and hydrogen has been examined by experiments with a modified Wilson expansion apparatus. The observations are interpreted in accordance with Lenard's theory (*Sitzungsber. Heidelberg Akad.*, 1914, 29).

According to older experiments, the condensation may give rise to a comparatively small number of droplets or to the formation of fog, and these phenomena require different degrees of expansion which are, however, characteristic for a particular vapour–gas mixture. The author's experiments, on the other hand, lead to the conclusion that the two types of condensation cannot be differentiated by any definite expansion values and that there is no evidence of any real discontinuity. It would therefore seem that the various types of condensation nuclei are not of uniform size, but that there is a more or less continuous variation in the dimensions of the nuclei in each particular group.

It has been further found that the largest condensation nuclei are the ions formed under the influence of terrestrial radiation. The number of these nuclei depends on the nature of the vapour and of the admixed gas. According to the experiments with air, the number of such charged nuclei in 1 c.c. is about 900.

In addition to the above, the experiments show the existence of a relatively very small number of uncharged nuclei of large size which begin to be effective when the degree of supersaturation is five. It is probable that these nuclei are the result of chemical changes brought about by the highly penetrating terrestrial radiation. By far the greater number of the uncharged nuclei are of smaller dimensions. For the most part they consist of polymerised molecules of the vapour, which contain two or three simple molecules. The number of such polymerised molecules is calculated to be $1{\cdot}9 \times 10^{-11}\%$ for water, $2{\cdot}5 \times 10^{-11}\%$ for ethyl alcohol, and $0{\cdot}8 \times 10^{-11}\%$ for benzene. These correspond respectively with 110,000, 340,000, and 190,000 nuclei per c.c.

The nature and number of the uncharged nuclei thus depend on the chemical nature of the vapour, but are not appreciably affected by the admixed permanent gas.

When the vapour-gas mixtures are submitted to β- or γ-rays from a radium preparation, uncharged nuclei of greater dimensions are produced than those normally present. The number and size of these increase with the intensity of the radiation.

The experimental observations are said to be in complete agreement with Lenard's views of the nature of the condensation process. In particular, the results support the view that there is a certain degree of supersaturation for every vapour which will bring all the nuclei into action as condensation centres. H. M. D.

Steam Distillation. F. J. TROMP (*J. Soc. Chem. Ind.*, 1917, **36**, 276).—The author has had occasion to distil considerable quantities of aniline in steam, and finds that very rapid and efficient condensation of the distillates is secured when the tube from the distillation vessel is led into a tank of water which can be cooled by a suitable cooling coil. The distillate is syphoned off periodically. Once the air has been completely expelled from the distillation vessel and connexions, there appears to be practically no limit to the rate at which steam can be passed, and condensation is complete as long as the liquor in the tank is below its boiling point.

H. W.

Heats of Vaporisation and Maximum Vapour Pressures. A. LEDUC (*Compt. rend.*, 1917, **164**, 494—497).—The author has calculated the values of the latent heat of vaporisation, L, from the Clapeyron-Thomson formula, $L = T/J(u' - u)dF/dT$, in the case of ether and benzene. Taking the values of Ramsay and Young (compare *Phil. Trans.*, 1887, **178**) for the maximum pressure of ether between 0° and 60°, the values calculated for L do not agree with the experimental values according to Winkelmann (compare A., 1880, 692). There is a better agreement in the case of benzene at 80°. W. G.

Atomic Volumes of Oxygen and the Halogens at the Critical Point. GERVAISE LE BAS (*Chem. News*, 1917, **115**, 146—147).—A comparison of the atomic volumes of free and combined oxygen at the critical temperatures of the various substances concerned shows that the volume is three times that of hydrogen with the exception of alcoholic oxygen, the atomic volume of which is twice that of hydrogen. The relative volume of the halogens compared with hydrogen are at the critical temperatures: fluorine, 2·3; chlorine, 6·0; bromine, 7·7; iodine, 10·4. H. M. D.

Internal Friction of Chlorinated Aliphatic Hydrocarbons. W. Herz (*Zeitsch. Elektrochem.*, 1913, **23**, 24).—The author has calculated from the specific viscosity measurements previously published (Herz and Rathmann, A., 1913, ii, 835) the absolute viscosities (*C.G.S.*) and the specific volumes. The following values are obtained: *cis*-dichloroethylene, 25°, $\rho=0·003901$; *trans*-dichloroethylene, 25°, $\rho=0·004553$; 50°, $\rho=0·003690$; trichloroethylene, 25°, $\rho=0·005490$, $v=0·6878$; 50°, $\rho=0·004466$, $v=0·7078$; 75°, $\rho=0·003709$, $v=0·7288$; tetrachloroethylene, 25°, $\rho=0·008391$, $v=0·6219$; 50°, $\rho=0·006567$, $v=0·6380$; 75°, $\rho=0·005335$, $v=0·6551$; tetrachloroethane, 25°, $\rho=0·01614$, $v=0·6297$; 50°, $\rho=0·01118$, $v=0·6450$; 75°, $\rho=0·008185$, $v=0·6611$; pentachloroethane, 25°, $\rho=0·02171$, $v=0·5984$; 50°, $\rho=0·01482$, $v=0·6117$; 75°, $\rho=0·01060$, $v=0·6255$. From these values the Batschinsky function between fluidity and specific volume can be confirmed.

J. F. S.

A Method for the Determination of Dissociation Pressures of Sulphides and its Application to Covellite (CuS) **and Pyrites** (FeS_2). E. T. Allen and Robert H. Lombard (*Amer. J. Sci.*, 1917, [iv], **43**, 175—195).—The method described depends on the balancing of the dissociation pressure of the sulphide against the vapour pressure of sulphur at a known temperature. In the application of this method, the sulphide and sulphur are contained in bulbs at opposite ends of an evacuated combustion or quartz tube. This tube is heated by a pair of coaxial cylindrical furnaces which are attached to carriages, so that the two furnaces may be easily slipped over the experimental tube and brought tightly end to end when an experiment is to be made. The bulb containing the sulphide is heated in the one furnace at a measured temperature, and by trial the temperature is ascertained at which the vapour pressure of the free sulphur in the other bulb is equal to the dissociation pressure of the sulphide. To facilitate the carrying out of this determination, the heating of the sulphide furnace is arranged so that the temperature throughout is as uniform as possible, whilst the sulphur furnace is heated in such a way that the temperature rises continuously from the outside to the inside end. By moving the carriages it is thus possible to make a series of observations with the sulphur bulb at various temperatures. The gain or loss of sulphur by the sulphide may be determined by the appearance, by analysis, or by making use of some physical property.

The method has been applied in the measurement of the dissociation pressures of covellite and pyrites over a range of 1 mm. to 500 mm. The dissociation pressure of covellite was thus found to increase from 1·5 mm. at 400° to 510 mm. at 490° and that of pyrites from 0·75 mm. at 575° to 518 mm. at 680°. An advantage of the method is that the equilibrium may be approached from above and below, and the observer is consequently not likely to be deceived by false equilibrium phenomena. It has the disadvantage of requiring a considerable time, and cannot be used when the dissociation pressure is much greater than atmospheric.

The method may be applied to compounds other than sulphides provided that there is only one volatile dissociation product which does not attack glass or quartz and condenses at accessible temperatures. It also affords a convenient means for synthesising dissociating compounds. H. M. D.

Diameter (of Molecules) and Solubility. W. Herz (*Zeitsch. Elektrochem.*, 1913, **23**, 23—24).—Making use of the previously calculated molecular diameters of organic liquids (Herz, A., 1915, ii, 682), the author now examines the connexion between this quantity and the solubility of these liquids in water. It is shown that generally the solubility is greater the smaller the diameter. Thus at 18°, 100 grams of solution contain 25 grams of methyl acetate (diameter $=0·94 \times 10^{-8}$), 5 grams of methyl propionate (diameter $= 1·04 \times 10^{-8}$), and 1·7 grams of methyl butyrate (diameter $=1·16 \times 10^{-8}$). The same is found with isomeric substances, which, although possessing equal molecular weights, yet have different molecular diameters; for example, propionic acid is completely miscible with water, whilst methyl acetate dissolves to the extent of 25 grams in 100 grams of the saturated solution. The diameters are: propionic acid, $0·63 \times 10^{-8}$; methyl acetate, $0·94 \times 10^{-8}$. This relationship is, however, not absolute, and can be entirely altered by specific chemical properties. J. F. S.

Non-, Uni-, and Bi-variant Equilibria. XII. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 816—824. Compare this vol., ii, 132, 169).—A further discussion of the possible number of types of pressure–temperature diagrams, in which it is shown that although three types may be, in general, distinguished, the number is increased to four provided that two indifferent phases occur in the invariant point. Similarly, quaternary systems are generally characterised by four possible types of pressure–temperature diagrams, but in case there are two indifferent phases in the invariant point, the number of such types increases to twelve. The types in question are symbolically represented and divided into three groups.

H. M. D.

Four-component Systems. H. E. Boeke (*Zeitsch. anorg. Chem.*, 1916, **98**, 203—222).—A general theoretical paper on the process of crystallisation in four-component systems, based on the tetrahedral representation of such systems, with special reference to the case of magmas. C. H. D.

Studies of the Carbonates. II. Hydrolysis of Sodium Carbonate and Sodium Hydrogen Carbonate and the Ionisation Constants of Carbonic Acid. CLARENCE ARTHUR SEYLER and PERCY VIVIAN LLOYD (T., 1917, **111**, 138—158).—The uncertainty attaching to previous determinations of the constant characteristic of the second stage in the ionisation of carbonic acid is probably due, for the most part, to errors involved in the assumptions made with respect to the degree of ionisation of sodium hydrogen carbonate and sodium carbonate. The difficulties incidental to the determination are discussed, and a new method is described which avoids the assumptions which have been made in earlier attempts to obtain the value of this constant.

If k_2 and k_3 are the first and second ionisation constants of carbonic acid, k_w the "constant" for water, α and β the degrees of ionisation of sodium hydrogen carbonate and sodium carbonate respectively, k_c the apparent value of the ratio

$$C^2_{NaHCO_3}/C_{Na_2CO_3}\,.\,[H_2CO_3],$$

and k_d the apparent value of $C_{NaHCO_3}\cdot[OH']/C_{Na_2CO_3}$, then $k_c=k_2\beta/k_3\alpha^2$ and $k_d=k_w\beta/k_3\alpha$. From experiments with dilute solutions of sodium carbonate (+hydrogen carbonate) in equilibrium with atmospheric carbon dioxide, in which the carbonate and hydrogen carbonate concentrations were determined by titration and the hydrogen ion concentration by hydrolysis of ethyl acetate, k_c and k_d have been determined. Since k_2 and k_w are known, the value of α may be got from the two previous equations by eliminating k_3, when $\alpha=k_2k_d/k_wk_c$. It is thus found that the degree of ionisation of sodium hydrogen carbonate is very nearly the same as that of sodium acetate.

The value of k_c increases with the dilution, and its maximum value is taken to represent k_2/k_3, from which β may be calculated by means of the equation $\beta=k_c\alpha^2/k_2/k_3$. The value of β may be represented by the empirical formula $\beta=1{\cdot}104-0{\cdot}320\log c$, where c is the sodium concentration in milligram equivalents per litre. There is evidence to support the view that β refers to ionisation in two stages rather than to ionisation represented by $Na_2CO_3=2Na^{\cdot}+CO_3'$.

The experimental data lead to $k_3=4{\cdot}91\times10^{-11}$ for the second ionisation constant of carbonic acid at 25°, when the value for the first ionisation constant is taken as $k_2=3{\cdot}5\times10^{-7}$ (Kendall, A., 1916, ii, 512) and $k_w=0{\cdot}82\times10^{-14}$. H. M. D.

Kinetic Theory of Reaction Velocity. A. MARCH (*Physikal. Zeitsch.*, 1917, **18**, 53—59).—A theoretical paper in which the author discusses the kinetics of the dissociation of a compound gas. It is assumed that dissociation occurs when the energy exceeds a certain critical value. If k is the velocity coefficient, then the influence of temperature on the velocity may be represented by the equation $d\log k/dT=A/T^2+B/T+d\log dE/(dt/dT)$, in which dE represents the average value of the deviations of the energy during the interval of time dT from the mean energy content characteristic of the temperature T, and A and B are constants.

If dE/dt is constant, this formula becomes identical with that put forward by Kooy. The theory also leads to the conclusion that there is a certain critical temperature above which a chemical compound is incapable of existence. This temperature can be calculated from the heat of formation of the compound.

H. M. D.

The Landolt Reaction. J. Eggert (*Zeitsch. Elektrochem.*, 1917, **23**, 8—19).—The author has evolved a theory to explain the time reaction occurring between iodates and sulphites in acid solution. This theory shows the connexion between the time of the reaction and the concentration of the reacting substances. In its chief points, the theory is confirmed experimentally; it is shown that the time of reaction is independent of the concentration of the sulphite ion, inversely proportional to the square of the iodate ion, and inversely proportional to the square of the concentration of the hydrogen ion. This last relationship only holds over a fixed range of concentrations. The time of the reaction is dependent only on two independent constants, k_1 and k_2, which are characteristic of the two main reactions, $3H_2SO_3 + HIO_3 = 3H_2SO_4 + HI$ (k_1), $5HI + HIO_3 = 3I_2 + 3H_2O$ (k_2), and can be experimentally determined. The time of reaction (T) can be calculated with satisfactory approximation by the formula $T = 1/(k_2 - k_1) . \log_e k_2/k_1$. The inexactitudes of the theory are theoretically discussed. The influence of potassium iodide is to accelerate the reaction, and this can also be quantitatively calculated on the basis of the present theory. A number of experiments are described which show the influence of the concentration of the sulphite ion, iodate ion, and hydrogen ion on the rate of the reaction; a further series of experiments on the influence of the iodide ion is also described. The author regards the Landolt reaction as a case of autocatalysis.

J. F. S.

Fundamental Atomic Weights. Alois Bilecki (*Zeitsch. anorg. Chem.*, 1916, **98**, 86—96).—It has been shown by the author that many atomic weights are multiples of the number 0·31. Oxygen, however, does not fall into this arrangement, but it is now shown that if instead of the ratio $16:0{\cdot}31 = 51{\cdot}612$ the approximate ratio $16:52$ or $4:13$ be taken, new regularities are found. This ratio has the value $0{\cdot}307692\dot{3}$, and may be called n. Taking the atomic weights of silver and bromine as $108 = 351n$ and $80 = 260n$ respectively, the deviations are well within the limits of the experimental error. Reducing this to the international value for silver, 107·88, bromine becomes 79·9111, n then becoming $n_1 = 0{\cdot}30\dot{7}35042\dot{7}$. The following ratios are then obtained: $Ag = 351n_1$, $Br = 260n_1$, $Cl = 115\frac{3}{8}n_1$, $I = 413n_1$. Many elements with even valency are derived from n, and many with odd valency from n_1. The atomic weights of cobalt and nickel and of thorium and ionium differ by $1n$.

C. H. D.

The Latest Revisions of the International Table of Atomic Weights. Ph. A. Guye (*J. Chim. phys.*, 1916, **14**, 449—461).—A criticism of the annual reports issued by the International Committee on Atomic Weights. Apart from the fact that the changes recommended by the Committee do not appear to be warranted in many cases by the actual facts, it is claimed that the recommendations are not based on the application of any obvious general principles. The author puts forward a number of considerations which might with advantage be taken into account in the issue of future annual tables. When changes are recommended, the reasons should be clearly stated, and the relevant experimental data included in the report. Unless special circumstances require that the atomic weight of an element should be altered, it would be better for various reasons to revise the table every ten years instead of annually. H. M. D.

Isaac of Holland and Jan Isaac of Holland. W. P. Jorissen (*Chem. Weekblad*, 1917, **14**, 304—310).—An account of the work of two Dutch alchemists. A. J. W.

A Simple Apparatus for the Washing of Gases. Harold Heath Gray (T., 1917, **111**, 179—183).—The extraction of hydrocarbon or other vapours from mixtures in which the vapours are associated with permanent gases is usually effected by washing the gas by means of some liquid in which the vapour is readily soluble. The usual forms of "liquid" washers have the common drawback of interposing considerable resistance to the passage of the gas, but this difficulty is avoided by the use of a "vapour" washer, in which the gas to be washed is passed through a mass of condensing vapour of the solvent.

The washer described consists of a water-jacketed tube fitting tightly into the neck of a flask containing the heated solvent. The gas to be washed enters the flask through a narrower tube passing down inside the water-jacketed tube, which has an outlet for the washed gas at its upper end. The gas, heavily charged with vapour of the solvent, passes from the flask into the annular space between the inner tube and the water-cooled tube, where the vapour of the solvent is condensed and the substance to be estimated is thereby removed. The efficiency of the process is mainly due to the ideally intimate contact between the gas and the washing medium, but another important factor is that the solvent is continually present in large excess and in pure condition.

The apparatus has been employed for the extraction of toluene from coal-gas, in which case benzene may be employed as the "vapour" washing solvent. H. M. D.

A Removable, Universal Condenser. Vigreux (*Bull. Soc. chim.*, 1917, [iv], **21**, 46—48).—A description of a simple form of reflux condenser which can be used with different flasks without the use of a cork for fitting it. Its efficacy is claimed to be high. W. G.

Inorganic Chemistry.

The Ignition Point of Detonating Gas. ALEXANDER MITSCHERLICH (*Zeitsch. anorg. Chem.*, 1916, **98**, 145—166).—Dry detonating gas, prepared electrolytically, is passed through a tube heated by means of a large, gas-heated copper tube, the temperature being measured by quartz–mercury thermometers reading up to 650°. When highly diluted with inert gas, no noise of explosion is perceptible, but the ignition point may be fixed by the appearance of a flash in a darkened room, even when the action is insufficient to cause any perceptible movement of the mercury in the manometer.

The ignition temperature is higher, the lower the velocity of the gas in passing through the tube, when the latter is low. At higher velocities, the temperature is independent of the velocity. The formation of water takes place below the ignition point, to an extent which varies with the condition and previous treatment of the glass tube. Silica tubes bring about a still greater formation of water below the ignition temperature, whilst very little is formed in tubes of glazed, and especially unglazed, porcelain which has been previously heated for a long time at 700°. C. H. D.

Electrolytic Formation of Perchlorate. C. W. BENNETT and E. L. MACK (*Trans. Amer. Electrochem. Soc.*, 1916, **29**, 323—346).—The formation of perchlorate at the anode is the result of direct oxidation by active oxygen. Sodium chlorate is largely oxidised to perchlorate by means of sodium persulphate, the yield being increased by the presence of a silver salt or by removing sulphate as formed by means of barium oxide. Ozone oxidises a small, but distinct, proportion of chlorate to perchlorate. Acid solutions of permanganates are without effect. Hydrogen peroxide forms hydrochloric, but not perchloric, acid. This action is probably due to the liberation of a little chlorine from the chloric acid, which then reacts with the hydrogen peroxide. Oxygen activated by ultra-violet light has the same effect as ozone. C. H. D.

General Considerations Relative to the Physico-chemical Revision of the Atomic Weight of Bromine on the Basis of the Normal Density of Gaseous Hydrogen Bromide. PH. A. GUYE (*J. Chim. phys.*, 1916, **14**, 361—388).—The chemical methods which have been employed in previous determinations of the atomic weight of bromine are subjected to a critical analysis in which it is shown that further observations are required before it is possible to assign to bromine an atomic weight value which is of the requisite order of accuracy. The advantages of the density method as applied to hydrogen bromide are indicated, and by way of introduction to a series of investigations in which the density of hydrogen bromide has been determined with the greatest possible accuracy, the author gives an outline of improvements which have been effected in connexion with the experimental determination of gas densities and of the methods which may be most advantageously used in the reduction of the measurements of the density at pressures of 1, $\frac{2}{3}$, and $\frac{1}{3}$ atmosphere so as to obtain the ideal density which would be observed if the gas conformed absolutely to the requirements of the simple gas laws. H. M. D.

Revision of the Atomic Weight of Bromine. Determination of the Normal Density of Gaseous Hydrogen Bromide. ENRIQUE MOLES (*J. Chim. phys.*, 1916, **14**, 389—444).—The density of hydrogen bromide has been determined at 0° and at pressures of 1, $\frac{2}{3}$, and $\frac{1}{3}$ atmosphere, and from the data the molecular weight of hydrogen bromide and the atomic weight of bromine have been deduced.

The hydrogen bromide was prepared by four different methods: (1) hydrolysis of phosphorus tribromide, (2) action of bromine on hydrogen sulphide, (3) action of bromine on naphthalene, (4) action of bromine on paraffin. It was purified by chemical treatment and by liquefaction and fractional distillation, the efficacy of which process was increased by causing the gas to bubble through a portion of the liquefied substance between successive distillations.

Thirty-three determinations of the density at 0° and 760 mm. gave a mean value of 3·64442 grams for the weight of a litre of gas. The mean of eleven determinations at 506·67 mm. gave 2·42204 grams per litre, and the mean of seventeen determinations at 253·332 mm. gave 1·20737 grams per litre. When reduced to 760 mm. these became respectively 3·63314 and 3·62190 grams. From these numbers the coefficient of compressibility is calculated, and the value of λ in the expression $1+\lambda=(pv)_0/pv$ is thus found to be 0·00931. This number is employed in the calculation of the molecular weight of hydrogen bromide in terms of that of oxygen, for which $\lambda=0·00097$ and the weight of a litre at 760 mm. and 0° is taken as 1·42905. The molecular weight is thus given by $M=32\times 3·64442\times 1·00097/1·42905\times 1·00931=80·9333$. By taking $H=1·0076$, this gives for the atomic weight of bromine $Br=79·926$.

This value is somewhat greater than that given by the chemical methods used at Harvard: $Br=79·916$ for $Ag=107·880$ or $Br=79·909$ for $Ag=107·871$.

The ratio of the atomic weights of chlorine and bromine given by density measurements is 0·44367, which is identical with the value given by the Harvard determinations and by the measurements of Goldbaum and of Noyes and Weber. H. M. D.

The Revision of the Atomic Weight of Bromine. Density of Hydrogen Bromide Gas under Reduced Pressure. C. K REIMAN (*Compt. rend.*, 1917, **164**, 180—181. Compare this vol., ii, 137).—Numerous determinations were made of the weight of a litre of hydrogen bromide at 506·67 mm. and 253·33 mm. From these results the values of a normal litre of the gas were calculated, the values for the two series being 3·6330 grams and 3·6218 grams respectively. The variation from Avogadro's law between 0 and 1 atmos. is then calculated as being $1+\lambda=1{\cdot}00927$. From these results and those previously obtained (*loc. cit.*), the value for the atomic weight of bromine is deduced as 79·924, which is in close agreement with that obtained by Moles (A., 1916, ii, 314, 526; preceding abstract). W. G.

The Normal Density of Hydrogen Bromide Gas. W. J. MURRAY (*Compt. rend.*, 1917, **164**, 182—183).—The hydrogen bromide was prepared by the action of water on anhydrous aluminium bromide, carefully purified by fractional distillation. The mean of sixteen determinations gave the weight of a normal litre of hydrogen bromide as 3·6440±0·0005 grams, which is in close agreement with the values obtained by Moles (A., 1916, ii, 314, 526) and Reiman (this vol., ii, 137; preceding abstract). W. G.

A New Method of Determining the Atomic Weight of Iodine. MARCEL GUICHARD (*Ann. Chim.*, 1916, [ix], **6**, 279—318; 1917, [ix], **7**, 5—49).—A full account of work already published (compare A., 1914, ii, 723). W. G.

The Action of Ozone on Inorganic Iodine Compounds. E. H. RIESENFELD and F. BENCKER (*Zeitsch. anorg. Chem.*, 1916, **98**, 167—201).—Harries (A., 1912, i, 407) has assumed the presence of a new modification of oxygen, O_4, in ozone. The oxidising power of ozone towards iodine compounds has hitherto been examined only in acid, neutral, and alkaline solutions of potassium iodide. The reactions with iodine, iodates, and periodates have not been investigated. Ozone reacts with solutions of potassium iodide instantaneously, even below 0°, but the final equilibrium in the solution between $K^{\cdot}$, OH', I', IO', IO_3', and IO_4' is only attained after some days. The higher the concentration of the ozone in the oxygen used, the greater is the influence of the hydroxyl ions. In acid solutions the ordinary reaction is accompanied by one in which 3 atoms of oxygen from a molecule of ozone take part, the 'oxidation number' being independent of the ozone concentration, but increasing with the acid concentration and with falling temperature, the highest value actually obtained being 2·7. The higher reaction may be an addition of ozone to iodine ions, forming iodate, or a formation of hydrogen peroxide. In either case the product at once reacts with the excess of iodide, and free iodine is the final product. The value 1 is not much altered by the addition of salts.

Ozone is without action on neutral and acid solutions of potassium iodate, but in alkaline solution oxidation to periodate takes place. Ozone is without action on periodate. There is no evidence for the existence of a modification of oxygen containing more than three atoms, the differences observed by Harries between the results of gravimetric and volumetric estimations being due to the action of hydroxyl ions. C. H. D.

The Preparation of Fluorine from Hydrogen Fluoride or other Fluorides by Chemical Means. OTTO RUFF (*Zeitsch. anorg. Chem.*, 1916, **98**, 27—37).—The only chemical method for the preparation of fluorine is that of Brauner (T., 1894, **65**, 393) by heating the double salt, $3KF,HF,PbF_4$ (compare following abstract). This result has not been confirmed, the products of decomposition by heat being lead difluoride and platinum tetrafluoride when a platinum vessel is used. Liquid or gaseous silicon tetrafluoride is practically without action on the double salt, a small quantity of gas acting on potassium iodide–starch paper being obtained at 250°, but without altering the composition of the salt. A larger quantity is obtained by the use of antimony pentafluoride. Sulphur and iodine form sulphur fluoride and iodine pentafluoride respectively.

[With WILHELM PLATO.]—*Triammonium hydrogen plumbofluoride*, $3NH_4F,HF,PbF_4$, is prepared by dissolving lead tetra-acetate in concentrated hydrofluoric acid and adding ammonium hydrogen fluoride, filtering, and evaporating. The salt may be heated at 190° under atmospheric pressure or even under 10 mm. pressure without change, but in a good vacuum decomposition takes place at 100°, nitrogen being evolved.

[With GEORG WINTERFELD.]—It has not been found possible to prepare lead tetrafluoride by the action of sulphuric acid on Brauner's double salt, or by the action of hydrofluoric acid under various conditions on lead tetra-acetate. C. H. D.

The Preparation of Fluorine from Tripotassium Hydrogen Plumbofluoride by Chemical Means. BOHUSLAV BRAUNER (*Zeitsch. anorg. Chem.*, 1916, **98**, 38—46. Compare preceding abstract).—The differences between the results obtained by the author in 1894 and those of Ruff are not explained. The earlier lead preparation contained manganese, which may have acted as a catalyst, or the gas evolved by heating may not have been fluorine. It is, however, shown that silicon does not inflame spontaneously in dry hydrogen fluoride. C. H. D.

New Determination of the Atomic Weight of Tellurium. ARTHUR STÄHLER and BRUNO TESCH (*Zeitsch. anorg. Chem.*, 1916, **98**, 1—26).—Tellurium is best purified by fractional distillation, which removes nearly all impurities except antimony. Conversion into chloride and distillation of the product removes many impurities, including antimony. For the investigation, tellurium is first distilled twice in a vacuum, converted into the tetrachloride, and fractionally distilled in a stream of chlorine, the latter operation being repeated five times. The tetrachloride is dissolved in concentrated hydrochloric acid, diluted, and precipitated by sulphur dioxide, the precipitating vessel being enclosed in an autoclave under 18—20 atmospheres pressure to ensure complete reaction. The amorphous product is dried, fused, and fractionally distilled in a good vacuum, electrolytic hydrogen being used to fill the apparatus. The temperature being near to the softening point of Jena glass, the final distillation is performed in a silica tube. The tellurium obtained in this way, from three different sources, in all cases proves to be spectroscopically free from impurities.

Tellurium is converted into the dioxide by dissolving in nitric acid and heating in a stream of dry air, the basic nitrate then being decomposed by heat. The nitric acid which distils over is collected and evaporated, and yields a further small quantity of tellurium dioxide. The value obtained for the atomic weight (O = 16) is 127·513 ± 0·003. C. H. D.

Tellurium Perchlorate. FR. FICHTER and MAX SCHMID (*Zeitsch. anorg. Chem.*, 1916, **98**, 141—144).—Iodine perchlorate having been previously obtained (A., 1915, ii, 253), the attempt has now been made to prepare tellurium perchlorate. Tellurium dioxide dissolves readily in warm concentrated perchloric acid to a clear solution, which deposits glistening, hexagonal leaflets on cooling. These are drained, washed with anhydrous alcohol out of contact with air, and dried in a stream of dry air. For analysis, the salt is decomposed by means of warm sodium acetate solution, the tellurium dioxide collected in an alundum crucible and dried, and perchlorate estimated in the filtrate by precipitation with nitron. The analysis is also controlled by reduction to tellurium by means of hydrazine hydrate.

Tellurium perchlorate has the composition $2TeO_2,HClO_4$, corresponding with the known basic nitrate, $2TeO_2,HNO_3$. It may be heated to constant weight at 300° without decomposition.

C. H. D.

Phospham. F. W. DAFERT and ALFRED UHL (*Zeitsch. landw. Versuchs-Wesen, Österr.*, 1916, **19**, 389—392; from *Chem. Zentr.*, 1917, i, 162).—The authors have endeavoured to determine whether oxides of nitrogen are actually formed during the oxidation of phospham, and, if so, to what extent the formation occurs. The crude material, prepared according to the directions of Liebig and Wöhler, was used, since the complete purification of phospham has not yet been effected. For the experiments, weighed portions of the finely-powdered material were mixed in a porcelain boat with the requisite oxidising agent and heated in a glass or porcelain tube. The escaping gases were bubbled through standard potassium hydroxide solution. Of the oxidising agents employed (BaO_2, $PbCrO_4$, PbO_2, MnO_2, $KMnO_4$, CuO, etc.), silver oxide was found to give the most uniform results and also to act at a comparatively low temperature. In these circumstances, exactly one-half of the nitrogen contained in phospham is eliminated in the form of nitrogen compounds, whilst the other half is evolved in the elementary condition. This is probably accounted for by the difference in the mode of linking of the nitrogen atoms in the phospham molecule, $N{:}P{:}NH$. Phospham is not greatly changed in the soil, and cannot serve as a source of nitrogen or phosphorus for plants. H. W.

Compounds of Arsenious Oxide and Salts. III. F. A. H. SCHREINEMAKERS and (MEJ) W. C. DE BAAT (*Chem. Weekblad*, 1917, **14**, 244—248. Compare this vol., ii, 173).—An investigation of the behaviour of arsenious oxide with haloids of the alkali and alkaline-earth metals. The chlorides of lithium, sodium, calcium, and strontium, and the bromides of calcium and strontium, do not form compounds. The chlorides of potassium, ammonium, and barium, the bromides of lithium, sodium, potassium, ammonium, and barium, and potassium iodide yield derivatives of varying composition. A. J. W.

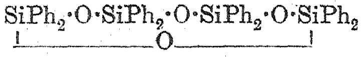
Boric Anhydride and its Hydrates. JAMES ECKERSLEY MYERS (T., 1917, **111**, 172—179).—The relations between boric anhydride, metaboric acid, and orthoboric acid have been examined.

When a potassium iodide–iodate solution is added to a solution of orthoboric acid, iodine is liberated after one or two minutes. When solutions of boric anhydride and metaboric acid are similarly treated, iodine is liberated much more slowly, and in some cases it was found that two or three hours were required to produce the same effect as that obtained with orthoboric acid. Some specimens of metaboric acid react more quickly than others, and it is suggested that this may be due to a difference in the molecular complexity.

Further information relative to the hydration of boric anhydride was obtained by observations on the rate of increase in weight of the substance when exposed in a thin layer to an atmosphere saturated with water-vapour at a constant temperature. The results obtained show that the hydration takes place in two stages, the formation of metaboric acid in the first stage taking place much more quickly than that of orthoboric acid in the second. Other experiments by the same method with metaboric acid show that the progress of the hydration may be satisfactorily represented by the equation for a unimolecular change.

A study of the dehydration of orthoboric acid at about 100° has afforded evidence that metaboric acid is produced at a rate consistent with the equation for a unimolecular change. At higher temperatures the dehydration seems to result in the formation of molecular complexes of metaboric acid. H. M. D.

Nomenclature of Silicon Compounds. ALFRED STOCK (*Ber.*, 1917, **50**, 169—170. Compare A., 1916, ii, 319).—Perhaps the greatest confusion in the nomenclature of silicon compounds is to be found in the case of substances containing the –Si–O–Si– system. It is proposed to call the parent hydrogen compounds of this type "siloxanes," and to specify the number of silicon and oxygen atoms in such terms as "disiloxane," "disildioxane," etc. For example, $(SiCl_3)_2O$ would be the formula of "hexachlorodisiloxane," and the compound,



$$\underbrace{SiPh_2\cdot O\cdot SiPh_2\cdot O\cdot SiPh_2\cdot O\cdot SiPh_2}_{O}$$

would be "octaphenyltetrasiltetroxane." It is not proposed to modify the accepted terminology in the case of polysilicates and polysilicic acids. J. C. W.

Silicon Chemistry and Carbon Chemistry. ALFRED STOCK (*Ber.*, 1917, **50**, 171—182).—From the fact that about five hundred compounds of silicon are now known, exclusive of the silicic acids and silicates, the question can be discussed whether the earlier chemists were justified in believing that it only required time and opportunity to develop a silicon chemistry analogous to that of carbon, or whether Moissan was right in denying such a close analogy. The material is now reviewed in an interesting manner under the headings of the following linkings: Si–H, Si–C, Si–Hal., Si–N, Si–Si, Si=Si, Si–O, and Si–O–Si, and the well-known differences between carbon and silicon in such combinations are emphasised.

Perhaps the chief reason why it has been possible to extend carbon chemistry so enormously is the fact that the affinity of carbon is about equally strong for positive and negative non-metallic elements (for example, H, O, S, N, Cl, or C). Although the maximum valency of silicon is also four with regard to both hydrogen and oxygen, yet there is an enormous difference between the positive and negative affinities. The affinity for oxygen is so predominant that practically all other silicon linkings are broken down by the action of cold water.

A further difference between carbon and silicon which would account for many of the divergences in the two series is that the four valencies are symmetrically distributed in carbon, but not in silicon (compare Barlow and Pope, T., 1908, **93**, 1554). J. C. W.

The Reactivity of Silica with the Oxides of Calcium, Barium, and Magnesium in the Solid State. J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1916, **98**, 57—69).—The reactions between these oxides have been investigated by means of heating and cooling curves. Lime and precipitated silica react at 1011°, but the reaction comes to a standstill owing to the formation of a layer of metasilicate. A more vigorous reaction begins shortly above 1400°, owing to the eutectic temperature of the lime–silica system being reached. The reactivity of other varieties of silica diminishes in the order: silica glass, cristobalite, quartz. Calcium carbonate is acted on to a small extent by precipitated silica at or below 900°, possibly owing to the presence of a larger proportion of small particles, but the lime formed at the dissociation temperature is not specially reactive. Precipitated silica reacts with barium oxide at 900°, whilst no arrest has been observed on the heating curve of a mixture of silica and magnesia. C. H. D.

Carbon Oxysulphide, COS. ALFRED STOCK and ERNST KUSS (*Ber.*, 1917, **50**, 159—164).—Carbon oxysulphide may be obtained by the action of hydrochloric acid on commercial ammonium thiocarbamate, according to the equation $NH_4{\cdot}CO{\cdot}S{\cdot}NH_2 + 2HCl = COS + 2NH_4Cl$. In order to purify it, it is bubbled through 33% sodium hydroxide to absorb carbon dioxide and hydrogen sulphide, dried by means of calcium chloride and phosphoric oxide, then condensed by means of liquid air, and finally fractionated.

The pure gas is odourless and does not at once give a precipitate with barium hydroxide or copper sulphate solution. It is slowly decomposed by water, but in the dry state it is permanent even in sunlight.

It has D^{-87° 1·24, m. p. −138·2° (CO_2, −56·4°, CS_2, −112·1°), b. p. −50·2°/760 mm. (CO_2, −78°; CS_2, 46°). One part of water dissolves 0·54 vol. at 20°, 1 part of alcohol dissolves 8 vols. at 22°, and 1 part of toluene 15 vols. at 22°.

It is slowly and regularly absorbed by 33% sodium hydroxide (about 2% per minute), much more readily by an 8% solution (33% per minute), or by a 23% solution of potassium hydroxide (8% per minute). It is therefore quite possible to estimate readily absorbable gases in the carbon oxysulphide by using 33% sodium hydroxide, and allowing for the loss of the latter gas during the time of the absorption. J. C. W.

Sodium Arsenites. F. A. H. SCHREINEMAKERS and (MEJ) W. C. DE BAAT (*Chem. Weekblad,* 1917, **14**, 262—267, 288—290). —An application of Schreinemakers's graphic method to the equilibria in the system water–arsenious oxide–sodium hydroxide at 25°. A. J. W.

Water Content of Crystalline Sodium Tetraborate. J. HOFFMANN (*Chem. Ind.*, 1916, **39**, 411—412; from *Chem. Zentr.*, 1917, i, 304).—Estimation of the loss of water of crystallisation of sodium tetraborate at different temperatures has shown that the first five molecules begin to be lost below 100°, whilst six molecules are lost at 100°; the seventh and eighth molecules escape at 130°, the ninth at 150°, whilst the tenth is evolved at 160° and above. At the ordinary temperature crystalline borax has the formula $Na_2B_4O_7,10H_2O$; at 100°, $Na_2B_4O_7,5H_2O$; at 130°, $Na_2B_4O_7,3H_2O$; at 150°, $Na_2B_4O_7,2H_2O$; at 180°, $Na_2B_4O_7,H_2O$. The penultimate molecule of water of crystallisation is retained more firmly than the others, and prolonged heating is necessary to remove it. Borax of the composition, $Na_2B_4O_7,H_2O$, exists in traces far above this temperature, but below 318° the bulk of the water is driven off. When it is desired to obtain practically anhydrous borax in the non-glassy form, the crystalline material is heated at 318° (m. p. of potassium nitrate). Absolutely anhydrous borax is difficult to obtain in the non-glassy state, since the dehydrated powder absorbs water more readily than the glassy material. The latter during five months only absorbs 0·4% of water, whilst this amount is absorbed by the former in twenty-four hours. After sixteen months the powdered form had absorbed 10, the glassy 0·6, molecules of water. H. W.

The Internal Field of the Lithium Atom. A. HARTMANN (*Physikal. Zeitsch.*, 1917, **18**, 14—16).—According to Watts, the line series of the alkali metals are most satisfactorily represented by the Mogendorff–Hicks formula. By neglecting the smaller coefficients this passes into the Balmer formula, and from this it would seem that the structure of the lithium atom is similar to that of the hydrogen atom. If this be the case, two of the three electrons are probably in close proximity to the positive nucleus, and take no part in the emission of the characteristic radiation.

By assuming that the internal electric field is symmetrical and by making use of Bohr's theory relative to the nature of the emission phenomenon, the author has calculated the magnitude of the force due to the action of the nucleus on the rotating electrons when the number of these is one, two, and three respectively. From the result the apparent charge of the nucleus is derived, and for the three cases referred to it is found that the charge is represented by e, $5/4e$, and $(1+1/\sqrt{3})e$ respectively. The result of the calculation is considered to be favourable to the view that the lithium atom contains a single active electron, the two others being in relatively close proximity to the positive nucleus and neutralising thereby two-thirds of the positive charge. H. M. D.

Allotropy of the Ammonium Haloids. III. F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 798—804. Compare A., 1916, ii, 31, 431).—Further observations on the relation between the α- and β-forms of ammonium bromide show that the transformation is facilitated by the addition of glycerol, and in presence of this, the transition point, as determined by the thermal method, was found to lie between 137·3° and 139·5°. Measurements of the solubility of ammonium bromide in water at temperatures between 95° and 158° show evidence of two solubility curves intersecting at 137·4°, which agrees well with the value recently recorded by Smith and Eastlack (A., 1916, ii, 482). If x is the molar fraction of ammonium bromide in the saturated solution, the solubility below the transition temperature is given by $\log x = -372{\cdot}7/T + 0{\cdot}31978$, and above the transition temperature by $\log x = -293{\cdot}7/T + 0{\cdot}12727$. Measurements of the vapour pressures of the saturated solutions gave no evidence of a break at 137°, the vapour pressure at temperatures between 98° and 157° being satisfactorily represented by the equation $\log p = -1927{\cdot}6/T + 6{\cdot}8302$.

By means of thermal observations it has been found that ammonium iodide also exists in two forms, and that the transition point lies between −17·2° and −15·6°. The transformation appears to be accelerated by the addition of small quantities of water. It has been found possible to observe that transition point and the eutectic point for the system NH_4I-H_2O at −28° in the same cooling experiment. According to the observations of Smith and Eastlack (A., 1916, ii, 529), extending from −19° to 136°, there was no evidence of the existence of two modifications of ammonium iodide. H. M. D.

Synthesis of a Basic Calcium Salt, on the Ground of a Change of Properties of Milk of Lime. N. BUSVOLD (*Zeitsch. anorg. Chem.*, 1916, **98**, 202).—The power of milk of lime to resist settling is increased by the addition of calcium nitrate, a maximum value for the permanence being found at the composition $2CaO,Ca(NO_3)_2$. By slaking quicklime with a concentrated solution of calcium nitrate, white needles of the salt

$$2Ca(OH)_2,Ca(NO_3)_2,2H_2O,$$

are obtained, which become turbid on the addition of water.

C. H. D.

The Temperatures of Formation and Decomposition of the Carbonates of Calcium, Strontium, Barium, and Magnesium under a Pressure of One Atmosphere. J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1916, **98**, 47—56).—Dissociation temperatures may be determined more rapidly by taking heating and cooling curves than by measurements of pressure. Calcium carbonate gives a well-marked arrest on heating, but the contraction on formation of lime makes the mass so little reactive that the cooling curve is continuous. On increasing the surface of the lime by grinding, however, the absorption of carbon dioxide is hastened, and a corresponding arrest is found on the cooling curve. The dissociation temperature of calcium carbonate is thus found to be 913—923°, this being independent of the size of grain. The dissociation of strontium carbonate begins at 1141°, but only becomes rapid at 1255°. Barium carbonate only begins to dissociate at 1361°, its melting point. Magnesium carbonate dissociates at 546°. C. H. D.

Cadmium and Zinc Nitrites. PRAFULLA CHANDRA RÂY (T., 1917, **111**, 159—162).—Cadmium nitrite, prepared by trituration of cadmium chloride with silver nitrite, extraction with water, and evaporation in a vacuum, forms bright, pale yellow crystals of the composition $Cd(NO_2)_2$. According to conductivity measurements, the nitrite is appreciably less ionised than the chloride in $0{\cdot}1N$-solution. On the other hand, its ionisation is much greater than that of mercuric nitrite. The greater tendency of cadmium, as compared with mercuric nitrite, to form basic salts may be explained in terms of this difference in the ionisation of the two salts.

On heating, cadmium nitrite begins to decompose at about 150°. The main reaction compares with $3Cd(NO_2)_2 = 2CdO + Cd(NO_3)_2 + 4NO$, but some nitrite also decomposes amounting to $Cd(NO_2)_2 = CdO + NO + NO_2$.

The solution obtained by the interaction of zinc sulphate and barium nitrite evolves nitric oxide when concentrated by evaporation, and the residue consists of a basic zinc nitrate. H. M. D.

The Solubility of Lead Sulphate in Highly Concentrated and Fuming Sulphuric Acid. HUGO DITZ and FRANZ KANHÄUSER (*Zeitsch. anorg. Chem.*, 1916, **98**, 128—140).—The solubility of lead sulphate in highly concentrated sulphuric acid, as in the manufacture of acid by the contact process, is greater than appears in the literature. Acid of various concentrations is added to dry lead sulphate in stoppered bottles, and shaken from time to time, the solubility being determined after three days. The solution is filtered through asbestos by means of suction. The solubility increases with the concentration of the sulphuric acid, slowly up to 97%, then rapidly up to 100%, a discontinuity observed between 98·6% and 98·9% being possibly due to experimental error. From the maximum solubility at 100%, the curve falls to about 5% of free sulphur trioxide, where there is a minimum, after which it again rises rapidly to 15% of trioxide, and then less rapidly to 22%.

The known curve of electrical conductivity of sulphuric acid is very similar to the curve just described. The degree of attack of highly concentrated sulphuric acid on metallic lead also corresponds in general with the same curve. C. H. D.

Neodymium as the Cause of the Red-violet Colour in certain Minerals. EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1917, 7, 143—146).—The author shows that the reddish-violet colour of many minerals cannot be due to the presence of permanganates, as has been often assumed. The reasons advanced against the generally accepted view are: (1) permanganates can only be formed by vigorous reactions which would in many cases destroy the mineral; (2) many minerals showing a violet-red colour also contain ferrous iron, and consequently may be assumed to have been formed under reducing conditions; and (3) these minerals do not exhibit the characteristic absorption spectrum of the permanganates. A careful examination of reddish-violet-coloured minerals by means of a microspectroscope shows that these minerals all exhibit the absorption spectrum of neodymium compounds. This spectrum has been very clearly observed in brown apatite from Ontario, violet apatite from California, and in reddish-violet calcites. J. F. S.

The Passive State of Metals. C. W. BENNETT and W. S. BURNHAM (*Trans. Amer. Electrochem. Soc.*, 1916, **29**, 217—254).—The passive state of metals may be regarded as one in which solution takes place slowly. Faraday's oxide or oxygen theory was generally accepted until it was shown by Hittorf that passive chromium dissolved quantitatively in most solutions as a sexavalent ion. The evidence for and against the oxide explanation is now reviewed, with a full bibliography. The oxide may be regarded as forming a film which is rendered stable by adsorption into the metal. The oxide is usually unstable, and only becomes stable on adsorption. In the case of chromium, the oxide is not higher than CrO_3, and is probably $CrCrO_4$, or CrO_2, but in the further oxidation at the anode the higher oxide is formed, and chromium dissolves in the sexavalent state. The oxide of iron is not higher than FeO_3, and may be FeO_2.

A case of an unstable substance being rendered stable by adsorption is that of cupric hydroxide, which is not decomposed to oxide on boiling with water in presence of manganese sulphate, which is adsorbed by the precipitate, or when itself adsorbed by wool. Iron is made passive by dipping in a solution of potassium ferrate, and chromium by potassium chromate. Lead usually becomes passive by the formation of lead peroxide, but in concentrated sulphuric acid at a low temperature lead dissolves as a quadrivalent ion.

All the phenomena of passivity are explainable on this hypothesis. C. H. D.

The Corrosion and Electrical Properties of Steels. SIR ROBERT HADFIELD and EDGAR NEWBERY (*Proc. Roy. Soc.*, 1917, *A*, **93**, 56—67).—The steels, having uniformly rubbed surfaces prepared by means of emery, are coated with wax so as to expose a constant area, and after immersing in *N*-sulphuric acid, the overvoltage is determined (T., 1914, **105**, 2420). The electrodes are then washed, dried, again rubbed with emery, and their potential in *N*-sulphuric acid measured against a mercurous sulphate electrode. The sum of this single potential and the overvoltage at the lowest current density used is regarded as a measure of the resistance to corrosion. This is compared with the loss in weight when the same steel is exposed to the same acid solution, and with the tendency to rusting on exposure to the atmosphere of the laboratory. The electrical measurements correspond much more nearly with the atmospheric corrosion than do the losses on immersion in acid. No great accuracy is yet possible, and in certain cases, such as steel with more than 12% of chromum, which is quite unaffected by exposure to the atmosphere, both the electrical and the acid methods greatly underestimate the resistance to corrosion.

C. H. D.

Chromium Phosphate. ALFRED FRANCIS JOSEPH and WILLIAM NORMAN RAE (T., 1917, **111**, 196—202).—When equal weights of chrome alum and disodium hydrogen phosphate are mixed in cold solution, an amorphous precipitate of violet chromium phosphate is obtained. When allowed to remain in contact with the solution for a day or two, this is transformed into a crystalline modification of the composition $CrPO_4,6H_2O$. If the contact is prolonged for a week, the crystalline hexahydrate is converted into a green, amorphous tetrahydrate. This change also occurs in contact with pure water, but is accelerated by sodium phosphate or chrome alum, and is also influenced largely by the temperature. If the violet hexahydrate is heated or boiled with water, it is transformed into a green, crystalline tetrahydrate. If boiled with acetic anhydride, the hexahydrate forms a green, crystalline dihydrate. The crystalline di- and tetra-hydrates when heated to low redness are converted into black, anhydrous chromium phosphate. The densities of the crystalline hydrates were measured, and attempts made to determine the rate of dehydration.

Precipitation of a hot chrome alum solution with excess of disodium hydrogen phosphate gave a green, amorphous chromium phosphate, which rapidly lost water at the ordinary temperature until the composition $CrPO_4,4H_2O$ was attained. At 60° a further loss of 2 molecules of water took place, and on heating to dull redness a brown, amorphous chromium phosphate was obtained.

The behaviour of the hydrated and anhydrous forms towards mineral acids is described in detail, and reference is made to an abnormally great loss in the weight of platinum crucibles when heated in a gas furnace at 1100°, although no loss was found when heating took place in an electric furnace at the same temperature but with practically no air current.

H. M. D.

The Constitution of the Tin-Cadmium and Tin-Bismuth Alloys. ARMIN BUCHER (*Zeitsch. anorg. Chem.*, 1916, **98**, 97—127).—The alloys, after melting in a vacuum, are forced up into an evacuated tube sealed at the top, by admitting air into the outer vessel. By breaking away the glass, smooth rods are obtained. The electrical conductivity and its temperature-coefficient, and the thermo-electromotive force, are then determined, pure silver being used as the comparison metal. Tin and cadmium are reciprocally soluble to the extent of 3% in the solid state, the conductivity and thermo-electric curves being straight between those limits. The solubility of tin in solid cadmium falls with falling temperature. Microscopical examination confirms the above results.

Tin holds up to 14% of bismuth, and bismuth holds up to 1·5% of tin, in solid solution. The conductivity curve is of the expected form, but the temperature-coefficient curve and the curve of thermo-electromotive force exhibit strongly marked discontinuities at the eutectic composition. This appears to be connected with the microscopic structure, alloys on the tin side of the eutectic point being fine-grained, whilst those containing free bismuth are very coarse. C. H. D.

Equilibria between Titanium Dioxide and Carbon Dioxide, and between Silica and Carbon Dioxide, in Alkali, Lime-Alkali and Alkali-Aluminate Fusions. PAUL NIGGLI (*Zeitsch. anorg. Chem.*, 1916, **98**, 241—326. Compare A., 1913, ii, 1036).—For the investigation of the system K_2O–TiO_2–CO_2, pure titanium dioxide is added to potassium carbonate in a platinum crucible in a continuous stream of carbon dioxide. After equilibrium has been reached, the crucible is quenched and allowed to cool in a desiccator which does not contain carbon dioxide. Under similar conditions, less carbon dioxide is expelled by titanium dioxide than by silica. The solid phase formed is $K_2Ti_2O_5$, the reaction beginning in the solid state, but only becoming rapid at about 860°. Carbon dioxide is absorbed on cooling, so that equilibrium may be reached from both directions. Treatment with hydrochloric acid leaves only titanium dioxide, in the form of transparent pseudomorphs after the titanate. In the molten mass other titanates, probably K_2TiO_3, are formed.

In the system Na_2O–TiO_2–CO_2, the solid titanate readily separates from the fusion, and there is also loss of sodium carbonate by volatilisation. Carbon dioxide is also frequently evolved during solidification. The principal solid phase is $4Na_2O,5TiO_2=Na_8Ti_5O_{14}$, but a titanate, $Na_2Ti_3O_7$, is also formed, as well as Na_2TiO_3 at high temperatures. $Na_8Ti_5O_{14}$ crystallises in forms resembling augite. The refractive index is more than 1·74.

The silicates and titanates obtainable from fusions are comparable with hydrated salts, silica and titanium dioxide playing a part similar to water of crystallisation.

In the system Na_2CO_3–$CaCO_3$, the double salt, $Na_2CO_3,CaCO_3$, forms large crystals, m. p. 813°. Mixtures containing more than 50 mol. % of calcium carbonate deposit calcite as the second solid phase. The eutectic point between the double salt and the solid solution rich in sodium carbonate is at 786° and 40 mol. % $CaCO_3$, the solid solution curve passing through a maximum at about 870°. The eutectic point in the system K_2CO_3–$CaCO_3$ is at 755° and 40 mol. % $CaCO_3$, the solid solution curve being without a maximum. The compound $K_2CO_3,CaCO_3$ melts at 813°, and closely resembles the sodium compound.

In the system K_2O–CaO–TiO_2–CO_2, fusions containing an excess of calcium carbonate convert the whole of the added titanium dioxide into perowskite, $CaTiO_3$. Any excess of titanium above this proportion forms $K_2Ti_2O_5$. The facts are in accordance with the frequent occurrence of perowskite as a product of the contact metamorphosis of limestone. The corresponding sodium system is quite similar. The product when silica is added to potassium and calcium carbonates is the orthosilicate, Ca_2SiO_4, and when wollastonite, $CaSiO_3$, is added to the carbonate fusion it is converted into the orthosilicate. Ca_2SiO_4 and $CaCO_3$ may occur together as solid phases from the same fusion at about 850° under atmospheric pressure in carbon dioxide. When alumina is present, silica first acts on the carbonate as if alumina were absent, but the silicate then reacts with alumina, so that an alkali aluminosilicate crystallises, and the liberated alkali then recombines with carbon dioxide. With potassium carbonate, potash–nepheline, $K_2O,Al_2O_3,2SiO_2$, is the product from all fusions. Orthoclase is decomposed by alkali carbonate, forming potash–nepheline, the silica thus liberated forming alkali silicate. A ternary diagram for the system K_2O–Al_2O_3–SiO_2 is given. C. H. D.

Iso- and Hetero-polyacids. XIV. Heteropolyvanadates. ARTHUR ROSENHEIM and MARIANNE PIECK (*Zeitsch. anorg. Chem.*, 1916, **98**, 223—240. Compare this vol., ii, 35).—The ammonium salt obtained from diammonium hydrogen phosphate and vanadium pentoxide (Friedheim, A., 1890, 1067; 1894, ii, 193, 198) has the constitution $(NH_4)_7[P(V_2O_6)_6],13H_2O$, but loses ammonia on recrystallisation, forming $5(NH_4)_2O,P_2O_5,12V_2O_5,44H_2O$. The potassium salt is still more hydrolysed, the only product isolated having the composition $5K_2O.P_2O_5,10V_2O_5,50H_2O$, the conductivity of which indicates that it is $K_5H_2\left[P^{(V_2O_6)_5}_{O}\right],24H_2O$. The heptabasic ammonium salt forms a crystalline precipitate with cæsium chloride, having the composition $5Cs_2O,P_2O_5,10V_2O_5,27H_2O$. This and the corresponding rubidium salt (with $46H_2O$) contain 2 mols. of combined water.

The salts containing vanadium and tungsten all contain combined water. Thus, $2BaO,V_2O_5,4WO_3,13H_2O$ contains $1H_2O$ in combination; $2Ag_2O,V_2O_5,4WO_3,2H_2O$ contains 2 mols., and the guanidinium salt, $2(CH_6N_3)_2O,V_2O_5,4WO_3,H_2O$, 1 mol. This is also the case with the salts having the colour of dichromates. In the purple series, the ammonium salt is now found to be

$$5(NH_4)_2O,3V_2O_5,14WO_3,37H_2O,$$

containing 5 mols. of combined water. The guanidinium salt, $5(CH_6N_3)_2O,3V_2O_5,14WO_3,12H_2O$, contains 5 mols. of combined water. The cæsium salt contains 2 mols. of water of crystallisation and 5 mols. of combined water. C. H. D.

Volatility of Gold at High Temperatures in Atmospheres of Air and other Gases. W. Mostowitsch and W. Pletneff (*J. Russ. Metall. Soc.*, 1915, 410—431; *Met. and Chem. Eng.*, 1917, **16**, 153—154; from *J. Soc. Chem. Ind.*, 1917, **36**, 341). Fused samples of purified gold (0·2—0·5 gram) were placed in an unglazed porcelain or quartz boat and submitted to a stream of gas for measured intervals, extending up to two and a-half hours, while heated in a Heraeus furnace at temperatures between 1100° and 1400°. The metal was weighed before and after each experiment by means of a micro-balance. In atmospheres of oxygen, nitrogen, carbon monoxide, or carbon dioxide, no loss of weight could be detected at temperatures up to 1400°. With hydrogen, however, volatilisation was observed, amounting at 1400° after an interval of twenty-five minutes to 0·98 mg., corresponding with a loss of 0·25%. The vaporisation was accompanied by a deep red colouring of the silica boat and the heating tube, due to the formation of a colloidal solution of gold in the quartz. This action is analogous to similar phenomena shown by copper when heated in hydrogen, and leads to the supposition that, at temperatures above 1200°, an unstable hydride, such as Au_2H_2, is successively formed and decomposed. H. W.

Mineralogical Chemistry.

The Rôle of Inorganic Agencies in the Deposition of Calcium Carbonate. John Johnston and E. D. Williamson (*J. Geology*, 1916, **24**, 729—750).—The authors discuss the effects producible by variation of certain factors which affect directly the solubility of calcium carbonate, and thus induce its precipitation from aqueous solution. The factors concerned are the partial pressure of the carbon dioxide in the atmosphere, the temperature, and the concentration of the solution in respect of calcium. At a given temperature, the equilibrium between calcite and its saturated solutions is determined by the coefficient of solubility of carbon dioxide, the ionic solubility product, $[Ca^{\cdot\cdot}][CO_3'']$, the ionisation-coefficients of carbonic acid, and the coefficient of hydrolysis of calcium carbonate. The free and the total carbonic acid, that is to say, $[H_2CO_3]+[CO_3'']+[HCO_3']$, determine the degree of alkalinity or acidity of the solution as measured by $[OH']$, and no change can be made in any one of these quantities without affecting each of the others. At 16°, the solubility of calcite increases from 44 to 75 parts per million, when the partial pressure of the carbon dioxide increases from 0·0001 to 0·0005. Under atmospheric conditions for which the mean value of the partial pressure may be taken as 0·00032, th solubility decreases from 81 parts per million at 0° to 52 parts at 30°. A change in the partial pressure from 0·00032 to 0·00030, or an increase of temperature of 2°, would result ultimately in the precipitation of about 2 grams of calcite from every cubic metre of a solution saturated with it.

Comparison of the calculated solubilities with the available analytical data indicates that the warmer surface layers of the sea are substantially saturated with respect to calcite, and precipitation is consequently to be anticipated if there is a reduction in the partial pressure of the atmospheric carbon dioxide or a rise in temperature of the surface layers in question.

In regard to biological processes which result in the deposition of calcite, it is pointed out that the above-mentioned inorganic factors must be taken into account, no matter what may be the agency which is supposed to be directly responsible for the deposition. There are grounds for believing that calcareous organisms are more abundant the more nearly saturated the water is in respect of calcium carbonate, and it is suggested that the decreasing abundance of calcareous organisms toward the polar regions is a question, not only of the decrease of general vitality but also of the decreasing capacity of the organism to secrete calcium carbonate from colder sea-water in which the degree of unsaturation is greater than for the same water at a higher temperature.

Although arragonite is occasionally formed in nature, it is considered that pure arragonite cannot persist in contact with sea-water for any length of time. If, however, the arragonite takes up other substances in the form of a solid solution, and its solubility is thereby reduced below that of calcite, it is possible that such impure arragonite may be stable in contact with sea-water.

It is considered that the accurate determination of temperature, salinity, and free and combined carbonic acid in sea-water in a systematic way would have an important bearing on many outstanding biological and geological problems. H. M. D.

Posthumous Stratifications in "Principal" Anhydrite. M. Rósza (*Zeitsch. anorg. Chem.*, 1916, **98**, 327—332).—The "principal" anhydrite is the more recent anhydrite of the potash deposits. At Stassfurt this deposit is as much as 80 metres thick. It frequently contains posthumous lenticular and vein-like layers of other salts, analyses of which are given. The changes are partly due to the injection of plastic masses of salts under pressure and partly to chemical transformations. C. H. D.

Presence of Nickel and Cobalt in Chromites. S. Piña de Rubies (*Anal. Fis. Quim.*, 1917, **15**, 61—65).—An account of spectroscopic analyses of samples of chromite, some of which contained cobalt and nickel. A. J. W.

Analytical Chemistry.

Simple and Efficient Gas Absorption Apparatus. H. Droop Richmond and E. Hembrough (*J. Soc. Chem. Ind.*, 1917, **36**, 317).—A simple and efficient apparatus for the absorption of gases, such as carbon dioxide, can be made by fitting a tube 13—15 cm. long and about 4 mm. internal diameter, on which six to eight bulbs about 12 mm. in diameter have been blown and the ends of which are expanded into small funnels of about 12 mm. diameter, inside a tube of about 17 mm. internal diameter and 20 cm. long, the bottom of which is drawn out and sealed to an inlet tube of about 3 mm. diameter, bent in the form of a V. In this tube are placed 10—15 c.c. of absorbing liquid. The gas enters through the inlet tube and bubbles up through the bulb tube, passing from bulb to bulb and taking up some of the liquid which overflows from the upper funnel, while fresh liquid continually runs in to replace that carried up; in these circumstances the contact between gas and liquid is efficient. The apparatus is simple, easily made, easily cleaned, and not at all fragile. H. W.

Modern Views of Acid and Alkaline Reactions and their Application to Analysis. I. and II. Niels Bjerrum (*Zeitsch. anal. Chem.*, 1917, **56**, 13—28, 81—95).—I. The author discusses the expression of acid and alkaline reactions in terms of hydrogen-ion concentrations, the theory of indicators, and the influence of indicators on acidimetric estimations.

II. Deals with indicators and the theory of titration. W. P. S.

Estimation of Traces of Water in Alcohol. Nussbaum (*Schweiz. Apoth. Zeit.*, 1917, **55**, 99; from *J. Pharm. Chim.*, 1917, [vii], **15**, 230).—A mixture of equal volumes of absolute alcohol and light petroleum is homogeneous when heated slightly, but becomes turbid when cooled; the point at which the turbidity appears is sharply defined, but is raised by about 16° when the alcohol contains 1% of water. The presence of water in alcohol may therefore be ascertained, and its quantity estimated, by determining the temperature at which the alcohol gives a turbidity when mixed with an equal volume of light petroleum. It is necessary, however, to make preliminary tests with light petroleum and quantities of alcohol containing definite amounts of water, as the point at which the turbidity is observed depends on the kind of light petroleum used. W. P. S.

Catalytic Hydrogenation of Organic Compounds with Base Metals at the Ordinary Temperature. Removal of Halogens from Organic Halogen Compounds. C. Kelber (*Ber.*, 1917, **50**, 305—310. Compare A., 1916, ii, 309, 609).—Details are given of a method for estimating halogens in organic combination, in which the compound is shaken in an atmosphere of hydrogen with nickel prepared by heating basic nickel carbonate in a current of hydrogen at 310—320°. The medium is either water or dilute alcohol, rendered alkaline. The method appears to have certain advantages over a similar one described by Busch (A., 1916, ii, 534), in which palladinised calcium carbonate is the catalyst. Several analyses are recorded. J. C. W.

Volumetric Analysis of Hypochlorite Solutions used for Sterilising Water. Rapid Analysis of Hydrogen Peroxide. A. Bury (*J. Pharm. Chim.*, 1917, [vii], **15**, 189—195).—The method depends on the reaction between a hypochlorite and hydrogen peroxide according to the equation $NaOCl + H_2O_2 = NaCl + H_2O + O_2$; the volume of the oxygen liberated is equal to that of the chlorine obtained when the hypochlorite is treated with an acid. The reaction may also be used for estimating the strength of hydrogen peroxide solutions. To estimate the available chlorine in a hypochlorite solution, 1 c.c. of the latter is placed in a narrow, graduated tube, which is closed at the bottom and provided with a bulb and tubulure at the top, water is added until the graduated portion of the tube is nearly full, and then hydrogen peroxide up to the zero mark. The tubulure is closed with a rubber stopper carrying a short capillary; the outer end of this is closed with the finger, the tube is inverted, and its contents mixed. When gas ceases to be evolved, the finger is moved slightly to allow the liquid to escape and equalise the pressure, the tube is placed in its normal position, and the volume of the residual liquid noted. The volume of the liquid which has escaped is thus found, and this volume is equivalent to that of the oxygen formed. The tube is graduated so that the readings give directly the quantity of active chlorine per litre of solution. W. P. S.

The Analysis of Gases by means of Orsat's Apparatus, replacing Pyrogallol by Hyposulphites. L. Descamps (*Bull. Assoc. chim. Sucr. Dist.*, 1916, **34**, 34—36).—Alkaline pyrogallol can be satisfactorily replaced by a 10% solution of either zinc hyposulphite or sodium hyposulphite, the latter being made slightly alkaline with sodium hydroxide, for the absorption of oxygen. The absorption is rapid and complete after two or three contacts. The presence of a little indigotin in the solution of the sodium salt gives an indication when the reagent requires renewing. W. G.

Estimation of Ozone. David (*Compt. rend.*, 1917, **164**, 430—431).—A rapid method for the estimation of small quantities of ozone in the air or in water. The ozone is made to act on a known volume of *N*/100-ferrous ammonium sulphate solution in dilute sulphuric acid, and this is then titrated back with *N*/100-potassium permanganate solution. It is claimed that by this method 0·02 mg. of ozone can be estimated. The solution of ferrous ammonium sulphate at this dilution is not oxidised by air, even if a large volume of air is bubbled through it, unless ozone is present. W. G.

Use of Diphenylamine and Diphenylbenzidine for Colorimetric Estimations. L. Smith (*Zeitsch. anal. Chem.*, 1917, **56**, 28—42).—The coloration obtained with diphenylamine in the colorimetric estimation of nitric acid according to Tillmans' method (A., 1911, ii, 151) decreases in intensity when the tube containing the mixture is shaken. It is suggested that a volatile substance is formed by the oxidation of the diphenylamine and that the presence of hydrochloric acid has an influence on the formation of this substance. The stability and intensity of the coloration are at a maximum at the ordinary temperature. The composition of the reagent has an influence on the sensitiveness of the test; for quantities of nitric acid ranging from 0·1 to 3·0 mg. of N_2O_5 per litre the best results are obtained by the use of a reagent consisting of 0·04 gram of diphenylamine, 39 c.c. of water, and 68 c.c. of concentrated sulphuric acid; for from 1 to 25 mg. of N_2O_5 per litre the reagent should consist of 0·08 gram of diphenylamine, 20·5 c.c. of water, and 84 c.c. of sulphuric acid. Diphenylbenzidine behaves similarly to diphenylamine towards nitric acid, but its sensitiveness is about twice as great.

W. P. S.

Prevention of Loss of Ammonia in the Estimation of Nitrogen by Kjeldahl's Method. Alice Wolf-Joachimowitz (*Chem. Zeit.*, 1917, **41**, 87).—To prevent loss of ammonia when the acid digestion mixture is rendered alkaline previous to distillation, the sodium hydroxide is added as a concentrated solution which is introduced slowly so that it forms a layer below the acid solution. The two layers are mixed after the flask has been connected with the condenser and absorption apparatus.

W. P. S.

Estimation of Ammonia and Sulphur Compounds in Urine. Rich. Weiss (*Münch. med. Woch.*, 1916, **63**, 1547—1548; from *Chem. Zentr.*, 1917, i, 127. Compare A., 1916, ii, 163). —Malfattis's method of estimating ammonia in urine is recommended for use by physicians, and, for this purpose, a simple apparatus is described. A test-tube is expanded into a bulb at the bottom and etched to indicate 10 c.c. Urine is poured in up to the mark. A few drops of phenolphthalein are added, followed by *N*/10-sodium hydroxide solution until the pink colour is just permanent. The liquid is diluted with distilled water to a second mark, 2—3 drops of phenolphthalein are again added, and, subsequently, exactly neutralised formaldehyde solution (40%) until the liquid reaches a third mark. The red colour disappears; *N*/10-sodium hydroxide is now added until the colour recurs, each c.c. of alkali solution corresponding with 0·0017 gram of ammonia. The tube is graduated in tenths of a c.c. above the upper mark, so that the volume of alkali can be directly determined.

Approximate methods for estimating sulphur compounds in urine are indicated, and an apparatus is described for the determination of pre-formed and total sulphuric acid and of ethyl hydrogen sulphate. Apparatus for the qualitative and quantitative indentification of indican in urine is depicted. H. W.

Microchemical Detection of Carbon and Sulphur. F. Emich (*Zeitsch. anal. Chem.*, 1917, **56**, 1—13. Compare A., 1915, ii, 646).—For the detection of carbon in a substance, the latter is heated in a closed capillary in an atmosphere of oxygen and the resulting carbon dioxide is collected in calcium hydroxide solution, the end of the capillary being broken under the surface of this solution when the combustion is completed. The formation of calcium carbonate in the capillary is seen when the latter is observed under the microscope. A distinct reaction can be obtained from 0·0004 mg. of glycerol. Sulphur can be detected by heating similarly small quantities of substance with nitric acid in a closed capillary; the formation of barium sulphate, when the solution is treated with barium chloride, is observed under the microscope. W. P. S.

Estimation of Hardness in Water. Albrecht Heyn (*Öff. Gesundheitspflege*, 1916, **7**, 584—604; from *Chem. Zentr.*, 1917, i, 126).—The literature is reviewed and experiments are described which were undertaken with the object of examining the influence of different constituents of natural waters on the estimation of hardness according to the methods of Clark, Winkler, and Wartha-Pfeiffer respectively. It is shown that nitrates, nitrites, and ammonia have no influence. Increase in sodium chloride causes low results for hardness by Clark's method, but has no effect on the other processes. Comparatively large amounts of iron compounds render Clark's method useless, the values obtained being far too high; Winkler's process can scarcely be applied, since it yields low figures for calcium and magnesium, whilst Wartha-Pfeiffer's method easily gives high results. When comparatively large amounts of organic substances are present, Winkler's method is very inexact; the figures for calcium are too high, for magnesium far too low, so that the total hardness is low. Wartha-Pfeiffer's method is also useless, yielding much too high values, particularly in the presence of much magnesium. In general, it appears advisable to determine the carbonate hardness according to Wartha-Pfeiffer, and to estimate calcium and magnesium separately according to Winkler.

The following modified method of calculating the results is proposed: to determine the hardness in degrees, different factors depending on the relative proportions of calcium and magnesium are used instead of multiplying the c.c. of potassium oleate solution used by the factor 0·75 empirically determined by Winkler. When the ratio of the number of c.c. of potassium oleate solution required for the calcium to the number required for the magnesium is 3:1 or over, the volume required for the latter element is multiplied by 0·75; when the ratio lies between 3:1 and 2:1, the factor is 0·6; when under 2:1 it is 0·5. H. W.

Rapid Method for the Estimation of Magnesium. N. Busvold (*Chem. Zeit.*, 1917, **41**, 42).—The following method is suitable for the estimation of magnesium in limestone. From 5 to 10 grams of the sample are ignited in an electric furnace, cooled, dissolved in the least possible quantity of dilute hydrochloric acid (1 : 1), the solution is boiled, an excess of calcium carbonate is added, the mixture again boiled, filtered, and the insoluble portion washed. The filtrate is treated with 20 c.c. of "6% milk-of-lime," boiled, cooled, filtered, and the precipitate washed with water containing calcium hydroxide. The filter and precipitate are now transferred to a flask and boiled for five minutes with 300 c.c. of water and 40 c.c. of *N*/1-oxalic acid solution; the hot mixture is filtered and the precipitate washed with hot water. The filtrate, which contains magnesium oxalate and free oxalic acid, is cooled, and the free oxalic acid is titrated with *N*/5-sodium hydroxide solution, using methyl-red as indicator. Twenty-five c.c. of dilute sulphuric acid are now added, the solution is heated at 70°, and the total oxalic acid titrated with *N*/5-potassium permanganate solution. The difference between the quantity of total oxalic acid and that of free oxalic acid gives the amount combined with the magnesium; 1 c.c. of *N*/5-oxalic acid solution is equivalent to 0·004306 gram of magnesium oxide. W. P. S.

Electrometric Titration of Zinc with Ferrocyanide. F. RUSSELL VON BICHOWSKY (*J. Washington Acad. Sci.*, 1917, **7**, 141—143).—It is found that the *E.M.F.* of a platinum electrode placed in a solution of potassium ferrocyanide has a value of −0·08 volt; if to such a solution a solution of a zinc salt is slowly added, the *E.M.F.* slowly rises in a normal manner until a quantity of the zinc solution exactly equivalent to the ferrocyanide has been added. When this state is reached, the *E.M.F.* suddenly jumps to −0·40 volt, and remains approximately constant with further addition of zinc. If the process is carried out in the reverse manner, that is, the ferrocyanide is run into the zinc solution, the platinum electrode may have any *E.M.F.* between 0·0 and −0·5 volt, depending on the previous treatment. The reversible value of the platinum electrode of −0·45 volt may be obtained by charging it to 2 volts in a zinc solution. When this initial *E.M.F.* has been obtained the titration cited above may be carried out in the reverse manner, the *E.M.F.* dropping sharply at the end-point to −0·10 volt.

J. F. S.

Estimation of Mercury in Organic Compounds. J. E. MARSH and O. G. LYE (*Analyst*, 1917, **42**, 84).—When organic mercury compounds are heated with calcium oxide, as in the ordinary lime-combustion method for the estimation of mercury, the volatilised mercury is frequently contaminated with a tarry or crystalline distillate. This may be prevented by the addition of calcium sulphate to the contents of the combustion tube. The mercury compound should be mixed with about twice its weight of calcium sulphate and an excess of calcium oxide; traces of mercury vapour remaining in the tube at the end of the combustion may be expelled by a current of carbon monoxide obtained by heating a quantity of calcium oxalate which has been placed previously at the closed end of the tube. W. P. S.

Estimation of Small Quantities of Iron and Aluminium. Ragnar Berg (*Chem. Zeit.*, 1917, **41**, 50—52).—The method described is particularly intended for the estimation of iron and aluminium in foods and organic substances. After the organic matter has been destroyed by combustion, preferably by heating with sulphuric acid and nitric acid (compare A., 1912, ii, 603), the acid solution containing the mineral substances is rendered alkaline with ammonia, then just acid with hydrochloric acid, a small quantity of ammonium acetate is added, the solution boiled, and the precipitate collected and washed with hot, very dilute ammonium sulphate solution. The precipitate is dissolved in hydrochloric acid, again precipitated as described, then dissolved once more in hydrochloric acid, the solution rendered ammoniacal, boiled, and the precipitate, consisting of iron and aluminium phosphates and silica, is collected, washed, ignited, and weighed. The silica is separated by fusion with potassium hydrogen sulphate, collected, and weighed; the solution containing the iron and aluminium phosphates is treated with ammonia, the precipitate obtained collected and washed, then dissolved in hydrochloric acid, the solution is transferred to a stoppered flask, zinc chloride added, the mixture is rendered alkaline with sodium hydroxide, then slightly acid with hydrochloric acid, and potassium iodide is added. The mixture is heated at 65° for twenty minutes, and the liberated iodine then titrated with $N/250$-thiosulphate solution. One atŏm of iodine is equivalent to 1 atom of iron. The aluminium is found by difference. W. P. S.

Estimation of Small Quantities of Cobalt. A. D. Powell (*J. Soc. Chem. Ind.*, 1917, **36**, 273—274).—Cobalt may be estimated by taking advantage of the fact that cobalt ammonium thiocyanate forms an intensely blue solution in amyl alcohol; in the presence of iron, the blue colour is masked by the red colour of ferric thiocyanate and the solution must be shaken with sodium carbonate or hydroxide to destroy the ferric salt, when the blue colour of the cobalt salt becomes apparent.

The author has applied this method to the estimation of cobalt in samples of pyrolusite containing 2% or more of iron oxide, and finds that the minimum concentration of ammonium thiocyanate necessary for complete extraction of cobalt is 25%; with lower concentrations, either the cobalt is not extracted from the aqueous solution by the amyl alcohol or, after extraction with the iron, the addition of sodium carbonate and consequent reduction in the concentration of the ammonium thiocyanate causes part of the cobalt to be re-extracted into the aqueous solution. A further difficulty is encountered in clarifying the amyl-alcoholic extracts previous to matching the colours; filtration through paper is inadmissable, as the colour is absorbed to a considerable extent and, even after long keeping, the extracts always contain sufficient ferric hydroxide in suspension to give a green shade. The trouble can be avoided by substituting sodium pyrophosphate for the sodium carbonate, except in cases in which manganese is present in such amount that the precipitate of manganese pyrophosphate renders extraction impossible.

The method thus modified has the advantages that the cobalt can be directly extracted, since the iron does not react with the thiocyanate if about half a gram of sodium pyrophosphate is present, and, further, that the extracts have a very uniform colour which remains unchanged during many months if the solution is kept in contact with a little sodium pyrophosphate. H. W.

Estimation of Nickel in the Presence of Zinc and Iron. S. Rothschild (*Chem. Zeit.*, 1917, **41**, 29—30).—Nickel cannot be deposited electrolytically from an ammoniacal solution with any degree of success when zinc or much manganese is present, although the process is trustworthy when the solution contains only iron and aluminium in addition to the nickel; deposition of nickel from a hot solution in the presence of sodium sulphite is untrustworthy in the presence of cobalt. Small quantities of iron are precipitated with the nickel when the latter is separated by means of dimethylglyoxime, and this contamination with iron is not prevented by the addition of a relatively large quantity of tartaric acid. It is therefore recommended that the nickel be precipitated in the usual way with dimethylglyoxime, the precipitate then dissolved in hydrochloric acid, the solution boiled for a few minutes with the addition of hydrogen peroxide, treated with an excess of ammonia, and the nickel deposited electrolytically from the solution. W. P. S.

Estimation of Chromium in Ferrochrome, Steel, and Slags by the Permanganate Method. P. Koch (*Chem. Zeit.*, 1917, **41**, 64).—About 0·25 gram of the finely divided sample is fused for twenty minutes in a porcelain crucible with 4 grams of sodium peroxide; when cold, the mass is boiled with water for thirty minutes, or until all the excess of peroxide has been decomposed; the mixture is then cooled, the ferric hydroxide is dissolved by the addition of sulphuric acid, excess of standardised ferrous sulphate solution is added, and this excess then titrated with permanganate solution. The ferrous sulphate solution may be standardised against $N/10$-potassium dichromate solution (4·9033 grams of the salt per litre), each c.c. of which is equivalent to 0·001733 gram of chromium. W. P. S.

Estimation of Small Amounts of Sugar in Urine. V. C. Myers (*Proc. Soc. Exper. Biol. Med.*, 1916, **13**, 178—180; from *Physiol. Abstr.*, 1916, **1**, 354).—Creatinine, uric acid, and probably other interfering substances, are precipitated with picric acid, as suggested by Folin; after that, a technique similar to that introduced by Benedict and Lewis for the estimation of sugar in the blood is employed. Full details of the method are given. Normal urine contains from 0·08—0·2% sugar. G. B.

Estimation of Sugar. N. SCHOORL and (MEJ.) A. REGENBOGEN (*Chem. Weekblad*, 1917, **14**, 221—229).—A reply to the criticisms of Ruoss (A., 1916, ii, 155) on the Fehling process for estimating sugars. The authors find that these substances can be satisfactorily estimated by the iodometric method of back-titration.

A. J. W.

The Influence of Pentoses in the Estimation of Reducing Sugars by means of the New Method of Heating at 63—65° for Ten Minutes (Mixture of the Cupropotassic Solution and the Liquid to be Analysed). H. PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1916, **34**, 21—24).—The pentoses, arabinose and xylose, both reduce the alkaline copper tartrate solution under the experimental conditions, but it is necessary to prolong the heating to forty minutes for the reduction to be complete. Where the pentoses are present, it is advisable to follow the method of Maquenne (compare A., 1916, ii, 156) and do trial estimations, always having the same amount of sucrose present. Another portion of the liquid is fermented, the sucrose and reducing sugars being destroyed, and the pentoses left are estimated directly. It is advisable for each analyst to fix his own conditions and prepare his own tables showing the values of differing amounts of each sugar in terms of copper or copper oxide under these conditions.

W. G.

The Estimation of Reducing Sugars in Sugar-cane Molasses and in the Fermented Liquid of these Molasses for the Estimation of the Fermented Sugars. H. PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1916, **34**, 24—28. Compare preceding abstract).—The author advocates the use of his method of estimating reducing sugars, by carrying out the reduction at 63—65° for ten minutes, claiming that, under these conditions, the action of the organic substances present is so diminished as to permit of the use of 1 gram of molasses for the direct estimation and 5 grams of the molasses after fermentation. W. G.

Muller's Process for the Destruction of Reducing Principles, permitting of the Direct Estimation of Crystallisable Sugar, specially applicable to the Products of the Cane-sugar Industry. CH. MULLER (*Bull. Assoc. chim. Sucr. Dist.*, 1916, **34**, 28—32).—The method is based on the use of Nylander's reagent (alkaline bismuth tartrate). Fifty c.c. of the sugar solution are heated on a water-bath for fifteen minutes with 5 to 15 c.c. of the reagent, according to the amount of reducing substances present. The liquid is cooled, 60 c.c. of basic lead acetate solution are added, the whole is made up to 300 c.c., shaken, filtered, and polarised in a 300 mm. tube. To 100 c.c. of the liquid 10 c.c. of 50% acetic acid are added, and the liquid again polarised. The liquid can be decolorised if necessary before polarisation. If more than 3 grams of reducing substances are present, proportionately more of Nylander's reagent must be added. The results obtained by this method are in close agreement with those from the longer and more complicated methods commonly used. W. G.

Glutose. H. Pellet (*Ann. Chim. anal.*, 1917, **22**, 43—47).—This carbohydrate is not fermented by yeast, and its quantity in molasses may be estimated by fermenting all the other sugars present and then taking the reducing power of the solution. One hundred grams of the molasses are diluted to 600 c.c., 1·5 c.c. of sulphuric acid added, then 50 grams of bottom fermentation yeast mixed with water, the whole mixture is diluted to 1 litre, and allowed to ferment for seventy-two hours. A portion of the solution is then treated with normal lead acetate, excess of lead is removed by the addition of sodium carbonate, and the cupric reducing power is estimated. The mixture of the Fehling solution and the solution under examination is heated at 65° for thirty minutes, the cuprous oxide then collected, dried, and weighed. The factor 1·008 is used to convert the weight of cuprous oxide found into glutose; the latter has about one-half the cupric reducing power of invert sugar. Sugar-cane molasses contain from 2·60 to 5·60% of glutose. W. P. S.

Qualitative Analysis of Carbohydrate Mixtures. J. M. Kolthoff (*Pharm. Weekblad*, 1917, **54**, 205—214).—A scheme for the detection of sucrose, lævulose, dextrose, lactose, dextrins, gums, amylum, and cellulose in mixtures of these substances. A. J. W.

Polarimetric Estimation of Starch in the Presence of other Optically Active Substances. C. Baumann and J. Grossfeld (*Zeitsch. Nahr. Genussm.*, 1917, **33**, 97—103).—The method described is particularly useful for the estimation of starch in products which contain starch paste, dextrins, and sugars, and depends on the fact that starch, whether raw or heated, is precipitated completely by lead tannate when the latter is formed in the starch solution. Ten grams of the substance under examination are shaken for 15 minutes (or for 1 hour if dextrins are present) in a 100 c.c. flask with 75 c.c. of water; 5 c.c. of 10% tannin solution are then added, followed by 5 c.c. of basic lead acetate solution, and the mixture is diluted with sodium sulphate solution to 100 c.c. After filtration, 50 c.c. of the clear filtrate are mixed with 3 c.c. of 25% hydrochloric acid and heated for 15 minutes in a boiling water-bath, then cooled; 20 c.c. of 25% hydrochloric acid and 5 c.c. of sodium phosphotungstate solution (12 grams of sodium phosphate and 20 grams of sodium tungstate per 100 c.c.) are added, the mixture is diluted to 100 c.c., filtered, and polarised in a 200 mm. tube. Another portion of 5 grams of the sample is heated directly with hydrochloric acid (compare Ewers' method, A., 1908, ii, 543) and the solution polarised after the addition of a further 20 c.c. of hydrochloric acid and clarification with sodium phosphotungstate. The difference between the two polarimeter readings is multiplied by 5·444 to obtain the percentage quantity of starch present; this factor is calculated from the average rotatory power of various starches, the average being $[\alpha]_D = +183·7°$. On account of the presence of acetates in the first part of the process, it is necessary to add 3 c.c. of hydrochloric acid, instead of 2 c.c. as given by Ewers, to bring the acidity of the mixture to the required concentration; the additional quantity of hydrochloric acid introduced after the inversion is for the purpose of insuring the complete precipitation of organic bases, alkaloids, etc., which may be present; sodium phosphotungstate fails to effect their entire removal from the more dilute hydrochloric acid solution. The error of the method does not exceed 0·2% when dealing with substances containing from 10 to 60% of starch together with large proportions of sucrose, dextrose, dextrins, milk, etc. W. P. S.

Analysis of Aspirin. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1917, [vii], **15**, 213—222).—The presence of acetic acid in the aspirin (*o*-acetoxybenzoic acid) molecule may be ascertained by treating the substance with an excess of calcium hydroxide, separating the insoluble calcium salicylate by filtration, and applying the usual tests for acetic acid to the residue obtained on evaporating the filtrate; it is necessary to ignite this residue at a low temperature in order to destroy remaining traces of salicylate before the tests are applied. Aspirin should not give a coloration with ferric chloride (absence of free salicylic acid), and should volatilise completely when heated. It should melt at 132°; in determining the melting point, the bath should be heated at about 125° before the capillary containing the substance is introduced, since aspirin tends to decompose and give a false m. p. when heated for some time at a temperature above 100°. To estimate the quantity of aspirin present in a sample, the acid and saponification numbers should be determined (compare Astruc, A., 1913, ii, 806). Samples of so-called aspirin examined by the author consisted of magnesium sulphate 53%, lactose 39%, and *o*-acetoxybenzoic acid and salicylic acid 8%. W. P. S.

Soluble Filters and Filtering Media. JOHN M. WILKIE and H. S. ANDERSON (*J. Soc. Chem. Ind.*, 1917, **36**, 272—273).—The use of soluble filters is discussed, the term being applied to filters in which both the medium and medium support are soluble in some arbitrarily selected liquid. For the separation of potash soaps from strong alcoholic mother liquors, a filter prepared as described below has proved very serviceable. A pear-shaped separator of 150—200 c.c. capacity is selected with a well-marked tubular portion between bulb and stopcock. Special potassium nitrate crystals are introduced, so as to give a column nearly filling the tube, and then 3—5 grams of powdered potassium nitrate which has been rubbed down smooth between paper just previous to use. The separator is finally tapped on the bench to consolidate the filter. The filter is then ready for use, and with alcoholic soap solutions no precautions are required other than seeing that the added liquor does not unduly disturb the surface of the potassium nitrate powder. In place of potassium nitrate, ammonium chloride may be used. H. W.

Estimation of the Alkaloids by Physico-chemical Volumetric Methods. Paul Dutoit and Meyer Lévy (*J. Chim. phys.*, 1916, **14**, 353—360).—The application of electrical conductivity measurements is recommended as furnishing a satisfactory method for the estimation of alkaloids. The method may be applied in several forms, according to whether the free alkaloid is neutralised by addition of an acid, or is displaced from its salts by the addition of a strong base, or is precipitated by the addition of one or other of the characteristic alkaloid reagents.

The first method is not of any real practical importance, but the second has been found to give quite satisfactory results with a number of alkaloids. Of the various specific alkaloid reagents which have been examined in connexion with the third method, the best results were obtained with silicotungstic acid. This acid is quite stable, and its conductivity remains constant even in very dilute solution. In applying the conductivity method with the use of silicotungstic acid to the estimation of alkaloids, the method followed is to add sodium acetate to the solution of the alkaloid salt, the concentration of which should be of the order $N/100$ to $N/1000$, the conductivity of the solution being then measured. Successive quantities of $N/2$- to $N/20$-solution of silicotungstic acid are then added, and the conductivity measured after each addition. The quantity of sodium acetate added should be such as to make its molar concentration from two to three times that of the alkaloid. The conductivity data when plotted give two intersecting curves, the point of intersection corresponding with the complete precipitation of the alkaloid. In most cases this is attained when the ratio of alkaloid to silicotungstic acid is as 4:1. H. M. D.

Colorimetric Estimation of Creatinine. L. Geret (*Zeitsch. Nahr. Genussm.*, 1917, **33**, 35—38).—The modification of the picric acid method described by Baur and Trümpler (A., 1914, ii, 595) yields about 33% more total creatinine than is found by the older method given by Baur and Barschall, and this difference in the quantities of creatinine found by the two methods does not therefore indicate that the quality or method of preparation of standard meat extracts have altered. W. P. S.

Identification of Opium with the Aid of Meconine and Meconic Acid. O. TUNMANN (*Apoth. Zeit.*, 1916, **31**, 499—500; 503—504; from *Chem. Zentr.*, 1917, i, 131—132).—Zinc chloroiodide is a suitable reagent for the microchemical detection of opium in broken pieces and dust; when the preparation is gently warmed with the reagent, the polygonal epidermal cells of the poppy capsule are well defined, the secondary membranes being coloured violet-blue, the primary deep yellow.

The meconic acid content of opium may fall as low as 1·5%. In using Autenreith's method of testing for meconic acid, it is necessary to filter the solution of magnesium meconate at the boiling point. In addition, it is frequently advisable to decolorise the aqueous solution of the residue obtained from the alcoholic extracts by means of benzene previous to boiling with magnesium carbonate. The maximum meconin content in opium in seven cases investigated was 0·112%. Little reliance can be placed on the sulphuric acid test for meconin.

The copper, silver, ferrous, and pyridine salts of meconic acid are suitable for its microchemical detection. The copper salt forms 3—5—10 μ long, pale yellow, intermingled needles and rods with occasional nodules. Limit of sensitiveness, 40—50 μg. In spite of their smallness, the crystals shine brightly between crossed Nicols. The silver salt appears under the microscope as yellow, occasionally almost black, needles (diameter, 15—25 μ) grouped in clusters, less frequently as colourless crystals, of length up to 20 μ. In polarised light, the smaller nodules show a dark cross, the larger groups appear grey and greyish-brown. Extinction in the single crystals is parallel to the long axis. The limit of sensitiveness is 5 μg. The ferrous salt is prepared by adding a grain of dehydrated ferrous sulphate to a drop of meconic acid; the mixture is warmed until a pale red solution is formed. After five to ten minutes, the formation of reddish-brown nodules and single crystals is observed, the latter gradually forming aggregates. All the crystals glow red in polarised light and show strong pleochroism. Limit of sensitiveness, 15—20 μg. The pyridine salt forms long, fine, colourless, single, prismatic needles, occasionally grouped in sheaves; the mean length of the needles is 60—120 μ and mean breadth 2·3 μ. Between crossed Nicols they appear pale grey. Limit of sensitiveness, 50 μg. Lastly, the reactions with zinc chloroiodide, potassium bismuth iodide, and potassium iodide–iodine can be used. The former yields a yellow, amorphous precipitate, whilst the other reagents give yellow or yellowish-brown nodules and sun-like crystal aggregates which, with the last-named reagent, attain a diameter of 300—400 μ. H. W.

Estimation of Antipyrine. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1917, [vii], **15**, 97—105).—A volumetric process described by Bougault (A., 1899, ii, 193) for the estimation of antipyrine depends on the titration of the substance in alcoholic solution with iodine solution in the presence of mercuric chloride; this method is trustworthy provided that the iodine solution is standardised against pure antipyrine at the time it is used. Bougault has also stated (A., 1900, i, 312) that the weight of the precipitate of iodoantipyrine (which is formed when antipyrine in dilute sodium acetate solution is treated with iodine solution) is an approximate measure of the quantity of antipyrine present, but does not claim that the reaction is quantitative. The author finds that this gravimetric method is untrustworthy, although it has been adopted by the French Codex in preference to the volumetric method.

W. P. S.

Biochemistry of Tobacco. I. Critical Examination of the Methods of Estimating Nitrogenous Substances in Tobacco Leaves. G. Paris (*Staz. sperim. agrar. ital.*, 1916, **49**, 405—424; from *Chem. Zentr.*, 1916, ii, 1079—1080).—An examination of the most important methods given in the literature has shown that the ammonia-nitrogen is not completely precipitated by phosphotungstic acid in sulphuric acid solution, but is partly contained in the amino-nitrogen estimated by difference. Similarly, the general methods of estimating amino- and protein-nitrogen yield inexact results. The volumetric estimation of nicotine is accurate if certain precautions are taken. The following methods are proposed: Water, total nitrogen, and nicotine are estimated in the tobacco itself, total nitrogen, protein nitrogen, nicotine nitrogen, ammonia nitrogen, nitric acid nitrogen, and amino-nitrogen in the aqueous extracts. The latter are obtained by agitation for six hours with water at 30—35°. Total nitrogen is estimated according to Kjeldahl, nicotine by Bertrand and Javillier's method (by precipitation as silicotungstate and weighing the silica and tungsten oxide after igniton, etc.), soluble protein-nitrogen according to Stützer, ammonia-nitrogen by distillation under diminished pressure, nitric acid nitrogen by Schlœsing-Wagner's method. For the estimation of amino-nitrogen, the protein nitrogen in the extract is removed by basic lead acetate, the filtrate freed from lead by sulphuric acid, and the bases precipitated by phosphotungstic acid (10%), care being taken to avoid any excess. A portion of the filtrate is freed from sulphuric and phosphotungstic acids by means of baryta; the solution is made up to a definite volume and filtered; after removal of excess of baryta with carbon dioxide the filtrate is concentrated to 50—60 c.c. at a low temperature, care being taken to maintain neutrality by periodical addition of very dilute nitric acid. The solution is finally precipitated by freshly prepared, clear mercuric nitrate solution, an excess of the reagent being avoided. The precipitate is filtered, decomposed with sulphuric acid according to Kjeldahl, and the nitrogen estimated. The filtrate from the mercury precipitate contains traces of asparagine and other amides and aspartic acid which have escaped precipitation. It can be made alkaline and the liberated ammonia distilled under diminished pressure. H. W.

Detection of Albumin in Urine. Aufrecht (*Pharm. Zeit.*, 1917, **62**, 38).—Ten c.c. of saturated sodium chloride solution, acidified previously with a few drops of concentrated nitric acid, are placed in a test-tube, and the urine to be tested is poured on the surface of this solution; if albumin is present, a turbid ring forms at the junction of the two liquids. The test will detect the presence of as little as 0·01 gram of albumin per litre of urine.

W. P. S.

The Detection of Blood, especially by means of Malachite-green, and a New Test with Rhodamine. E. FULD (*Biochem. Zeitsch.*, 1917, **79**, 241—256).—The author gives a review of the various methods for detecting blood (in fæces, etc.) by means of guaiacum tincture, reduced solutions of malachite-green, phenolphthalein, etc. He finds as specially sensitive a reagent made from rhodamine B extra, prepared by dissolving 0·2 gram of the dye in 50 c.c. alcohol, adding 5 grams of zinc dust and 4 c.c. of 10% sodium hydroxide to the boiling alcoholic solution. Such a solution, on the addition of 3% hydrogen peroxide, gives a coloration with blood in a dilution of 1 in 10,000,000, and is much more sensitive than a solution produced by the reduction of malachite-green.

S. B. S.

Electrometric Method of Titration, and its Application to the Examination of Gastric Juices. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1917, **79**, 1—34).—For the purposes of titration, a special form of electrode is figured and described. It consists essentially of a tube ending in a glass bell, into the side of which is fused another tube containing mercury having a platinum wire fused into the lower end, which just dips under the liquid to be titrated. Into the former tube hydrogen is passed. Connexion is made between the liquid to be titrated and the other half-cell through an inverted test-tube containing a gel of saturated potassium chloride solution with 3% agar. This is connected with a saturated solution of potassium chloride, which in its turn is connected with the calomel half-electrode. A large number of curves are given representing the changes in the $[H^{\cdot}]$ concentration when solutions of various acids and mixtures of acids are titrated with $N/10$-sodium hydroxide. Similar curves are given to show corresponding changes when gastric juices are titrated, and the results are correlated with the changes in colours of indicators and the reaction of gastric juices towards Günzberg's reagent. As a result of the experiments, the author recommends the following methods of analysis of gastric juices: I. For exact analysis, (*a*). For estimation of free hydrochloric acid, the electrometric measurement of $[H^{\cdot}]$ in the juice. (*b*) For estimation of bound hydrochloric acid, either chemical methods or electrometric titration to the point $p_H = 6·5$. II. For approximate clinical methods, the following three titrations: (*a*) to the salmon-pink tint with dimethylaminoazobenzene; (*b*) to the citron-yellow colour of the same indicator; (*c*) to the change in phenolphthalein. S. B. S.

General and Physical Chemistry.

Refractometry of Solutions. Lucrecia M. Blanc (*Ann. Soc. Quim. Argentina*, 1916, **4**, 294—314).—The index of refraction of solutions of the chlorides, sulphates, and nitrates of ferric iron, chromium, cobalt, nickel, and manganese increases regularly with the concentration. A. J. W.

Phototropic Phenomena of the Sulphates of Strontium, Calcium, and Barium. José Rodríguez Mourelo (*Anal. Fis. Quim.*, 1917, **15**, 74—93).—An account of the influence of varying proportions of manganese and bismuth on the phototropic and phosphorescent properties of the sulphates of the alkaline-earth metals. A. J. W.

Triboluminescence. A. Imhof (*Physikal. Zeitsch.*, 1917, **18**, 78—91).—The phenomenon of triboluminescence has been examined in experiments with a large number of substances, the object in view being to ascertain the influence of the size of the crystals, of temperature, and water of crystallisation, and also of the chemical relations.

For a particular triboluminescent substance, the emission of light can only be observed if the size of the crystals exceeds a certain limiting value. This varies from 0·002 to 4 mm., according to the nature of the substance, the limiting size decreasing with increase in the intensity of the triboluminescent emission. This intensity decreases for the most part with rise of temperature, but some observations at -80° indicate that there is a maximum on the intensity–temperature curve for certain substances between this and the ordinary temperature. The influence of temperature varies considerably with the nature of the substance. Triboluminescence is still exhibited by phosphorescent substances when the temperature has been raised sufficiently high to inhibit the phosphorescent emission.

In addition to eighty-seven inorganic substances, 25% of which were found to be triboluminescent, the effect was also investigated in a number of minerals and amorphous substances. The results seem to show that triboluminescence is not shown by the elements. Amongst compounds, chemically related substances behave similarly in regard to the phenomenon. When the various crystalline hydrates of a particular substance are compared, it is found that the behaviour depends on the water content. For the most part, the highest hydrate shows triboluminescence, whereas lower hydrates are inactive, but there are exceptions to this rule.

The spectral character of the triboluminescent radiation has been examined in a large number of cases. The emitted light is blue in the case of about 50% of the substances examined and yellow or orange for about 25%. The colour varies to some extent with the temperature, the wave-length sometimes increasing and sometimes decreasing as the temperature rises. H. M. D.

Effect of Various Substances on the Photochemical Oxidation of Solutions of Sodium Sulphite. J. Howard Mathews and (Miss) Mary Elvira Weeks (*J. Amer. Chem. Soc.*, 1917, **39**, 635—646).—The influence of a number of substances on the photochemical oxidation of 0·2*N*-solutions of sodium sulphite at 26° by ultra-violet light has been carefully examined. The reactions took place in quartz flasks, which were placed in a thermostat at fixed distances from the mercury lamp and constantly fed with air and stirred. A control reaction was carried out alongside the reaction under investigation. It is shown that copper sulphate has no appreciable effect on the velocity, pyridine strongly inhibits the reaction; methyl acetate and ethyl acetate also inhibit the reaction, but to a much smaller extent. Benzaldehyde, quinol, phenol, quinine sulphate, sucrose, and glycerol all inhibit the reaction, whilst carbamide has practically no effect whatever. The action of quinol decreases as the action proceeds, probably due to the decomposition of it by the light. Curves of the whole of the reactions with those of the accompanying controls are given in the paper.

J. F. S.

A Comparison of Radium Standard Solutions (continued). J. Moran (*Trans. Roy. Soc., Canada*, 1916, [iii], **10**, 77—84. Compare A., 1915, ii, 726).—The deterioration of the standards with repeated use is now ascribed to faulty experimentation, and the regeneration of deteriorated standards by addition to hydrochloric acid to the unsuspected presence of radium in the acid. In a new set of determinations, in which attention was paid to sources of error, no deterioration of the standards with use occurred. The Rutherford–Boltwood standards were found, in terms of the Washington standard, to be 96·4% for the weak and 97·3% for the strong.

F. S.

Attempt to Separate the Isotopic Forms of Lead by Fractional Crystallisation. Theodore W. Richards and Norris F. Hall (*J. Amer. Chem. Soc.*, 1917, **39**, 531—541).—Lead from Australian carnotite, containing 1 part of ordinary lead, 3 parts of radium-*G*, and a trace of radium-*B*, has been fractionally crystallised more than one thousand times as nitrate. The end fractions, least soluble and most soluble, were then purified and used for the determination of the atomic weight of the metal by means of the ratio $PbCl_2$:Ag. The following values were obtained: Pb (least soluble fraction) = 206·422; Pb (most soluble fraction) = 206·409. These values, it will be seen, agree to within 6 parts per 100,000, an amount which is inside the limits of experimental error. The β-ray activity of both end-fractions was also determined, and the values obtained agreed to within the experimental error of 1%. These observations indicate that the nitrates of radium-*D* and lead on the one hand and radium-*B* and lead on the other could scarcely be separated, if at all, by less than 100,000 crystallisations. Hence it may be inferred that the molecular solubilities of the nitrates are probably essentially identical. The outcome of the experiments gives strong experimental evidence in support of the hypothesis that isotopes are really inseparable by any such process as crystallisation. J. F. S.

The Explosive Potential in Carbonic Anhydride at High Pressures. CH. EUG. GUYE and C. STANESCU (*Compt. rend.*, 1917, **164**, 602—605).—The authors deduce the expression $V=F(m\,.\,d)$ for the value of the explosive potential in terms of m, the number of molecules in unit volume of the gas, and d the distance between the plates between which the discharge vibrates. This formula is verified for carbon dioxide at the ordinary temperature, with pressures varying between five and forty-five atmospheres and for distances between 0·34 mm. and 2·24 mm. The expression $V=F(m\,.\,d)$ thus applies to a gas compressed within limits much wider than those allowed by the Mariotte-Gay Lussac law.
W. G.

Disruptive Discharge in Compressed Gases. CH. EUG. GUYE and C. STANESCU (*Arch. Sci. phys. nat.*, 1917, **43**, 131—160). —A fuller account of work already published (compare preceding abstract). W. G.

Ion Adsorption Potentials. EMIL BAUR and S. KRONMANN (*Zeitsch. physikal. Chem.*, 1917, **92**, 81—97).—In a previous paper (*Zeitsch. Elektrochem.*, 1913, **19**, 590) measurements were recorded of potential differences at the surface of contact of aqueous and non-aqueous solutions, which were attributed to the adsorption of ions at the surface. Further measurements have now been made of the *E.M.F.* of cells in which two equally concentrated aqueous solutions of an electrolyte are separated by a non-aqueous liquid layer, a second electrolyte being added to one of the aqueous solutions. The cells examined were arranged according to the scheme:

$$N.E.\,|\,0{\cdot}01N\text{KCl}\,|\,A\,|\,B+0{\cdot}01N\text{KCl}\,|\,N.E.,$$

in which $N.E$ represents the normal electrode, A amyl alcohol which was chiefly used as the non-aqueous liquid, and B the foreign electrolyte, which consisted of sodium or potassium picrate or strychnine sulphate or chloride.

In consequence of diffusion, the *E.M.F.* of such cells changes with time, and this effect, as well as the influence of the concentration of the added picrate or strychnine salt, has been examined in detail. The general behaviour of cells of this type is quite consistent with the view that the contact potentials are due to the adsorption of picrate or strychnine ions. In particular, it is found that the relation between the *E.M.F.* and the concentration of the adsorbed ions in the solution is in agreement with the requirements of the adsorption formula. H. M. D.

Standard Cells and the Nernst Heat Theorem. F. M. SEIBERT, G. A. HULETT, and H. S. TAYLOR (*J. Amer. Chem. Soc.*, 1917, **39**, 38—52).—The authors have determined the specific heats of $CdSO_4,8/3H_2O$ and $CdCl_2,5/2H_2O$ over the temperature range

87° abs. to 274° abs., with the object of completing the data necessary for testing the Nernst heat theorem on the two standard cells, Cd(amalgam)|$CdSO_4,8/3H_2O,Hg_2SO_4$|Hg and Cd(amalgam)|$CdCl_2,5/2H_2O,Hg_2Cl_2$|Hg. The apparatus employed in the determinations and the method adopted were essentially the same as those of Nernst and Schwers (A., 1914, ii, 336). The experimentally determined values are expressed as functions of the temperature, the function being obtained with the aid of the Nernst–Linnemann specific heat equation. The values have been utilised along with other data obtained from the literature to investigate the thermodynamic relationships of the above-mentioned cells. Satisfactory agreement has been obtained between the calculated and the observed values with the assumption of Nernst for condensed systems and the consequent deduction that the integration constant in the thermodynamic equation is equal to zero. J. F. S.

Electromotive Force Developed in Cells containing Non-aqueous Liquids. J. M. NELSON and W. V. EVANS (*J. Amer. Chem. Soc.*, 1917, **39**, 82—83).—An account is given of some preliminary experiments which tend to show that the solution of a metal in acid is first preceded by the formation of an additive compound similar to the Grignard compounds. It is shown that the addition of magnesium ethyl bromide lowers the electrical resistance of ethyl ether and ethyl ether–benzene mixtures from 1×10^7 ohms to 9×10^2 ohms. The *E.M.F.* of cells of the type Mg|ether + C_2H_5Br + C_2H_5MgBr|Pt varies between 0·5 and 1·5 volts, whereas cells Mg|ethyl ether + C_2H_5Br|Pt could not be shown to possess any *E.M.F.* when first formed, but after keeping for some time an *E.M.F.* was set up due to the formation of the Grignard compound. Similar experiments were conducted with zinc and aluminium electrodes in place of magnesium, and instead of adding the Grignard compound a trace of iodine was added. Under these conditions each of these metals behaved exactly like magnesium. J. F. S.

The Absence of Thermal Hysteresis in the Copper–Constantan Thermo-element between 30° and 100°. T. W. RICHARDS and H. W. RICHTER (*J. Amer. Chem. Soc.*, 1917, **39**, 231—235).—It has been found that a highly sensitive copper–constantan multiple thermo-element shows no appreciable thermal hysteresis when subjected to rapid changes of temperature between 30° and 100°. The instrument is accordingly well adapted for certain types of accurate thermometric work. H. M. D.

The Application of the Theory of Allotropy to Electromotive Equilibria. III. Consideration of the Solubility of Metal and Electrons. A. SMITS and A. H. W. ATEN (*Zeitsch. physikal. Chem.*, 1917, **92**, 1—34. Compare A., 1916, ii, 77).—An account of the authors' views which have been for the most part published previously elsewhere (A., 1916, ii, 410, 597). H. M. D.

Applicability of the Ferro-Ferricyanide Electrode to the Measurement of the Activities of Electrolytes in Concentrated Solutions. G. A. LINHART (*J. Amer. Chem. Soc.*, 1917, **39**, 615—621).—A number of *E.M.F.* measurements of the ferro-ferricyanide electrode containing various concentrations of the two salts and various concentrations of potassium chloride (Linhart, this vol., ii, 13) against calomel electrodes have been made at 25°. It is shown that for given concentrations of potassium chloride the activities of the potassium ferro- and ferri-cyanides are proportional to their total concentrations. Concordant E_0 values are obtained by substituting the experimental values and those of Lewis and Sargeant (A., 1909, ii, 369) in the equation:

$$E_{\text{obs.}} = E_0 - 0{\cdot}05914 \log \{(K_4Fe[CN]_6)/(K_3Fe[CN]_6)(K^{\cdot})(Cl')\},$$

for concentrations of potassium chloride between $0{\cdot}2N$ and saturation, provided the approximately correct activity product of potassium and chloride ions is used. It is pointed out that since the E_0 values are fairly concordant for a definite range of concentration of electrolyte, the ferro-ferricyanide electrode can be used as a reference electrode for measuring activity products of many electrolytes. In addition to the measurements of activity products of simple ions, further work is contemplated on multivalent ions.

J. F. S.

Adsorption and Ionisation Equilibria. A. REYCHLER (*Kolloid Zeitsch.*, 1917, **20**, 81—83).—The Storch formula expressing the relation between the degree of ionisation of a strong electrolyte and the concentration of the solution is of the same type as the adsorption formula. It is suggested that this formal analogy may be an expression of the existence of some relation between the ionisation process and the adsorption of the ions and the non-ionised molecules of the electrolyte by the solvent.

H. M. D.

Correlation of Ionisation and Structure in Unsaturated Acids. C. G. DERICK and OLIVER KAMM (*J. Amer. Chem. Soc.*, 1917, **39**, 388—398).—The equivalent conductivities and ionisation constants of eight monocarboxylic naphthalene derivatives have been determined at 25° and the following values obtained: β-Naphthoic acid, $K_a = 6{\cdot}81 \times 10^{-5}$; Δ^1-dihydro-β-naphthoic acid (m. p. 118·5°), $K_a = 2{\cdot}91 \times 10^{-5}$; Δ^2-dihydro-β-naphthoic acid (m. p. 161°), $K_a = 2{\cdot}54 \times 10^{-5}$; Δ^3-dihydro-β-naphthoic acid (m. p. 101·2°), $K_a = 5{\cdot}70 \times 10^{-5}$; *ac*-tetrahydro-$\beta$-naphthoic acid (m. p. 96°), $K_a = 2{\cdot}45 \times 10^{-5}$; Δ^1-dihydro-α-naphthoic acid (m. p. 121·5°), $K_a = 7{\cdot}89 \times 10^{-5}$; Δ^2-dihydro-α-naphthoic acid (m. p. 86°), $K_a = 11{\cdot}44 \times 10^{-5}$; and *ac*-tetrahydro-$\alpha$-naphthoic acid (m. p. 85°), $K_a = 4{\cdot}40 \times 10^{-5}$. The place influence for a double bond in the Δ^2-position in respect to the carboxyl group has been shown to be a constant for the cyclic acids. Attention is directed to the dangers of drawing conclusions from the ionisation constants of unsaturated fatty acids where cis-trans-isomerism, due to the double bond, is possible. The place influence for a Δ^1 double bond has been shown to vary with the degree of conjugation, and it is suggested that a quantitative interpretation of Thiele's partial valency theory may be developed from this point of view. J. F. S.

Abnormal Electrolytic Dissociation. A. N. SACHANOV (*J. Physical Chem.*, 1917, **21**, 169—189).—The influence of concentration on the electrical conductivity of silver nitrate dissolved in liquids of varying dielectric capacity is discussed in reference to data previously published (A., 1915, ii, 729, 730). These data lead to the conclusion that the molecular conductivity, after correction for viscosity, shows a minimum at a certain concentration in all solvents. This concentration is largely determined by the dielectric capacity of the solvent, and increases with the magnitude of the dielectric constant. In proceeding from very dilute solutions, the molecular conductivity decreases at first with increasing concentration, reaches the minimum referred to above, and then increases as the concentration is further increased. This part of the conductivity–concentration curve corresponds with the so-called abnormal ionisation, which is attributed to the polymerisation of the electrolyte and the ionisation of the complex molecules.

Measurements of the *E.M.F.* of concentration cells with silver nitrate as the dissolved electrolyte and pyridine as solvent also afford support for the view that the degree of ionisation passes through a minimum value at a particular concentration.

Transport number measurements made with silver nitrate in various solvents show that the influence of the solvent on the value of the transport ratio diminishes with falling concentration, and in dilute solution the transport numbers are almost independent of the nature of the solvent. H. M. D.

Water Correction in Conductivity Determinations. JAMES KENDALL (*J. Amer. Chem. Soc.*, 1917, **39**, 7—24).—A theoretical paper in which the significance of the water correction in electrical conductivity determinations at very high dilutions, and the previous work on this subject are discussed. The method of deducing the exact "solvent correction," on the assumption that the water employed is in equilibrium with atmospheric carbon dioxide, has been worked out. It is shown that in the case of strong acids no correction is to be applied to the observed values throughout the ordinary range of dilutions. With acids weaker than acetic acid the correction to be applied becomes appreciable at very high dilutions. The correction in the case of exceedingly weak acids, for example, phenol, is considerable at all dilutions. In the case of bases the correction necessary is large and positive. In the case of salts of strong acids substantially accurate values are obtained by the Kohlrausch method—direct subtraction of the water conductivity. The ideal correction is slightly less than this, but only within the limits of experimental error. In the case of salts of weak acids, the true results lie between the uncorrected values and the water corrected values. The exact correction necessary varies with the concentration of the solution and the strength of the constituent acid. Hydrogen carbonates alone require no correction. The accepted values for Λ_∞ (as given by Kohlrausch) are, in the case of neutral salts, practically unaffected by the application of a carbonic acid correction to the conductivity data from which they are derived. Whether these salts follow the simple dilution law at exeedingly high dilutions is a point which cannot be satisfactorily established from the existing measurements. The confirmation of the figures of Kohlrausch, however, indicates that the equation of Kraus and Bray is applicable to neutral salts in very dilute aqueous solutions. The values of Λ_∞ derived by Kohlrausch for salts of weak acids are decidedly too low—in the case of sodium fluoride by almost 1%. J. F. S.

The Measurement of Electrolytic Conductivity. II. The Telephone Receiver as an Indicating Instrument for Use with the Alternating Current Bridge. EDWARD W. WASHBURN and KARR PARKER (*J. Amer. Chem. Soc.*, 1917, **39**, 235—245).—It has been found that a properly constructed telephone receiver is greatly superior for determining the setting in an alternating current bridge to all other instruments which have been proposed for the purpose. In most cases the degree of precision attainable in the measurement is finally controlled and limited by the temperature fluctuation of the thermostat. It is calculated that a precision of one part in 10 millions may be attained by a telephone receiver with an audibility current no smaller than 10^{-9} ampere, which degree of sensitivity is obtainable with telephones of a moderate price.

The tuning of a telephone receiver to the frequency of the current employed by mechanical, electrical, and acoustical methods is discussed, together with the variation of the sensitivity with the frequency and the determination of the audibility current.

H. M. D.

New Form of Conductivity Cell for Electro-titration. HAROLD E. ROBBINS (*J. Amer. Chem. Soc.*, 1917, **39**, 646—648).—A conductivity cell is described, which allows of easy access for the burette tip, and affords a means of mixing the two liquids. The electrodes are protected in a tube which is open at the top to admit the burette. The cell is connected at the bottom by means of a double right-angle bend with a bulb which has a slightly larger capacity than the cell itself. This is used for mixing, the whole of the liquid being drawn up into the bulb and mixed by passing a few bubbles of air through it. J. F. S.

Direct Reading Ionometer. F. E. BARTELL (*J. Amer. Chem. Soc.*, 1917, **39**, 630—633).—A potentiometer is described which, used in conjunction with a calomel electrode, enables direct readings of the hydrogen ion concentrations of solutions to be made between the limits 1×10^{-0}—1×10^{-14}, that is, for solutions varying in acidity from that of a normal acid to that of a normal base.

J. F. S.

Electrical Endosmose. I. T. R. Briggs (*J. Physical Chem.*, 1917, **21**, 198—237).—Previous observations relative to the phenomenon of electrical endosmose are discussed with reference to the electro-osmotic behaviour of solutions, and the various theories which have been advanced to account for electrical endosmose are subjected to a critical analysis.

In the author's opinion the most satisfactory working hypothesis is that advanced by Freundlich (*Kapillarchemie*, 1909, 245) and Bancroft (A., 1912, ii, 623), according to which the sign of the charge on a diaphragm depends on the relative adsorption of cations and anions, being positive if the cations are adsorbed to a greater extent than the anions, and negative if the reverse is the case. The development of this hypothesis leads to the conclusion that any change in the character of the adsorption will exert an influence on the electro-osmotic behaviour. The direction of electro-endosmotic flow indicates the sign of the charge on the diaphragm, and the rate of flow is proportional to the intensity of the charge if the potential gradient through the diaphragm is constant. Furthermore, it is held that the electrical endosmose furnishes a measure of the tendency of a solid to form an electrical suspension in a given liquid. It bears no relation, however, to the tendency of the solid to form non-electrical suspensions, such as are produced by the adsorption of solvent, solute, or neutral colloid. H. M. D.

Two Rules on the Connexion between some Physical Properties of Homologous Series of Organic Compounds. W. Herz (*Chem. Zeit.*, 1917, **41**, 183).—The product of the coefficient of expansion and the boiling point in absolute degrees is approximately a constant for the members of a given homologous series and does not vary much for the different series. The following mean values have been calculated for various series. Primary aliphatic alcohols, 0·0383; aliphatic monocarboxylic acids, 0·0446; aliphatic ketones, 0·0468; aliphatic ethers, 0·0487; aliphatic esters, 0·047; aliphatic *iso*-hydrocarbons, 0·0493; alkyl iodides, 0·0411; and aromatic hydrocarbons, 0·0421. The product of the specific heat at 20°, multiplied by the density at the same temperature, is approximately a constant for a given series, but varies considerably from series to series; thus for the following series the mean values are: aliphatic primary alcohols, 0·468; aliphatic hydrocarbons, 0·364; and aliphatic monocarboxylic acids, 0·557. It is noted that the specific heat continuously decreases as the series is ascended in the case of the alcohols and hydrocarbons, but in the case of the acids it alternately rises and falls. J. F. S.

The Le Chatelier-Brain Principle. Lord Rayleigh (T., 1917, **111**, 250—252).—In agreement with Ehrenfest (*Zeitsch. physikal. Chem.*, 1911, **77**, 2), the author considers that the principle is entirely ambiguous in its ordinary formulation, and that it is necessary to discriminate between the various parameters by which the condition of a system may be defined before the principle can be applied to yield definite results. H. M. D.

Determination of the Critical Temperatures and Pressures of Alkylamines and Alkyl Chlorides. A. Berthoud (*J. Chim. Phys.*, 1917, **15**, 3—29).—Using a modification of Pellaton's method (compare A., 1916, ii, 245) by means of which the critical temperature and pressure could be determined in one operation, the author has determined the values of these constants for five alkylamines and two alkyl chlorides. The results obtained and the values calculated for the constants a and b in van der Waals's equation are:

	t_c.	π (atmos.).	$10^5 . a$.	$10^6 . b$.
Methylamine	156·9°	73·6	1421	2675
Ethylamine.........	183·2	55·54	2113	3754
Propylamine	223·8	46·76	2988	4865
Dimethylamine ...	164·58	52·40	2069	3826
Diethylamine	223·3	36·58	3816	6216
Ethyl chloride ...	187·2	51·72	2318	4074
Propyl chloride ...	230·05	45·18	3170	5098

These values are, in general, considerably different from those obtained by Vincent and Chappuis (compare A., 1886, 963), and with these new values the anomalies, which have been shown to exist, for the amines, in several relations in which the critical constants enter, disappear. (Compare van Laar, A., 1916, ii, 386).

In an appendix the author considers the relationship between the constant a and the molecular weight in an homologous series, and shows, by reference to several series of compounds, that this ratio may, in certain cases, reveal polymerisation at the critical point. Various data are quoted which seem to indicate that ammonia is polymerised in the liquid state and at the critical point. He suggests that the fact that the nitriles satisfy Trouton's law, although they are polymerised, may be explained on the basis that the heat of dissociation of the complex molecules is very small.

W. G.

Improvements in Calorimetric Combustion, and the Heat of Combustion of Toluene. Theodore W. Richards and Harold S. Davis (*J. Amer. Chem. Soc.*, 1917, **39**, 341—354).—Improvements are described in the Berthelot calorimetric bomb in connexion with (1) the method of sealing the bomb; (2) the method of regulating and effecting the complete combustion of the substance under examination; (3) the method of igniting the substance and the automatic control of the temperature of the environment by a special synthermal regulator; and (4) the method of analysis of the residual gases for traces of unburnt carbon monoxide. The heats of combustion of naphthalene and of toluene have been determined and the following values obtained: naphthalene being taken as standard, 1 gram developed 9622 20°-calories and raised the temperature of the apparatus 3·616°; hence since 1 gram of toluene raised the temperature 3·821°, it has a heat of combustion 10,158 18°-calories, or 42·47 kilojoules per gram weighed in a vacuum.

J. F. S.

Thermal Chemistry of Pyridine. J. Howard Mathews, Ellis L. Krause, and Van L. Bohnson (*J. Amer. Chem. Soc.*, 1917, **39**, 398—413).—The heats of solution in pyridine of silver nitrate, silver thiocyanate, mercuric chloride, and mercuric iodide, and their compounds with pyridine, have been determined, and from the values obtained the heat of pyridination has been calculated. The method adopted was a modification of that previously used by Krause. The measurements were made in a Dewar vessel containing 400 grams of pyridine. The specific heat of every solution was determined by heating the solution electrically by a known amount of current and measuring the rise of temperature. All temperature measurements were made with a Beckmann thermometer. The specific heat of pyridine at 21° was found to be 0·3907. From the experimental data the following values were obtained, in which the symbol *py* signifies 200 molecules of pyridine: (1) $AgNO_3 + \mathit{py} = AgNO_3\mathit{py} + 17{,}036$ cal.; (2) $AgNO_3,3C_5H_5N + \mathit{py} = AgNO_3\mathit{py} - 2606$ cal.; (3) $AgNO_3 + 3C_5H_5N = AgNO_3,3C_5H_5N + 19{,}636$ cal.; (4) $AgNO_3,2C_5H_5N + \mathit{py} = AgNO_3\mathit{py} + 969$ cal.; (5) $AgNO_3 + 2C_5H_5N = AgNO_3,2C_5H_5N + 16{,}067$ cal.; (6) $AgNO_3,2C_5H_5N + C_5H_5N = AgNO_3,3C_5H_5N + 3569$ cal.; (7) $AgCNS + \mathit{py} = AgCNS\mathit{py} + 4364$ cal.; (8) $AgCNS,C_5H_5N + \mathit{py} = AgCNS\mathit{py} + 250$ cal.; (9) $AgCNS + C_5H_5N = AgCNS,C_5H_5N + 4114$ cal.; (10) $HgCl_2 + \mathit{py} = HgCl_2\mathit{py} + 13{,}387$ cal.; (11) $HgCl_2,\frac{2}{3}C_5H_5N + \mathit{py} = HgCl_2\mathit{py} + 4974$ cal.; (12) $HgCl_2 + \frac{2}{3}C_5H_5N = HgCl_2,\frac{2}{3}C_5H_5N + 8413$ cal.; (13) $HgCl_2,C_5H_5N + \mathit{py} = HgCl_2\mathit{py} + 1932$ cal.; (14) $HgCl_2 + C_5H_5N = HgCl_2,C_5H_5N + 11{,}455$ cal.; (15) $HgCl_2,2C_5H_5N + \mathit{py} = HgCl_2\mathit{py} - 5359$ cal.; (16) $HgCl_2 + 2C_5H_5N = HgCl_2,2C_5H_5N + 18{,}746$ cal.; (17) $HgCl_2,C_5H_5N + C_5H_5N = HgCl_2,2C_5H_5N + 7291$ cal.; (18) $HgI_2 + \mathit{py} = HgI_2\mathit{py} + 9974$ cal.; (19) $HgI_2,2C_5H_5N + \mathit{py} = HgI_2\mathit{py} - 4921$ cal.; (20) $HgI_2 + 2C_5H_5N = HgI_2,2C_5H_5N + 14{,}895$ cal. J. F. S.

Surface Tension. V. Structure of the Surfaces of Liquids, and Solubility as Related to the Work done by the Attraction of Two Liquid Surfaces as they Approach each other. William D. Harkins, F. E. Brown, and E. C. H. Davies (*J. Amer. Chem. Soc.*, 1917, **39**, 354—364. Compare A., 1916, ii, 222, 223).—The authors have determined the change of free surface energy when one square centimetre of interface is formed between two liquids. The measurements have been made between water on the one hand and a number of paraffins and the related cyclic hydrocarbons, olefines, halogen derivatives of the paraffins and benzene hydrocarbons, alcohols, acids, esters, amines, ethers, and mercaptans on the other. The temperature of the experiments varied between 10° and 40°. The data obtained indicate that at the interface between water and another liquid, the molecules in the surface of that liquid set themselves in such a way as to turn their most active or polar groups towards the surface of the water. At such surfaces, therefore, liquids show a structure. The decrease of free energy, when the surface of a second liquid approaches that of water (a polar liquid), depends primarily on the most active or polar group present in the molecule, and in a secondary way on the shape and size of the molecule. The solubility in water is related to this decrease of free energy, which more or less perfectly measures the attraction of the active group for the water molecule. Thus the presence of a very polar group, such as the carboxyl group, the carbonyl group, cyanide group, hydroxyl group, or the amide group, is sufficient to make the molecule of an organic substance soluble in water if the polar group does not have to pull into the solution a slightly polar group which is too long or too large. Whilst slightly polar groups, such as the methyl group, are attracted by water, the attraction is much smaller than that of the polar groups. The active groups cited above, and also ether, contain either oxygen or nitrogen atoms. The sulphur atom is much less active than these, but is much more active than the methyl group. Double or triple bonds between carbon atoms act as active groups, and benzene shows a much larger value for this decrease of free energy than the corresponding six carbon atom hydrocarbons which do not contain double bonds. True solubility is a molecular scale phenomenon, and is dependent on the attractions of the different parts of the various molecules for each other, and on the shapes and sizes of the molecules which must be fitted together to make a solution. The space occupied by a molecule depends on the extent of its kinetic agitation, so that the solubility of substances is highly dependent on temperature. J. F. S.

Surface Tension. VI. Orientation of Molecules in the Surfaces of Liquids. Energy Relations at Surfaces, Solubility, Adsorption, Emulsification, Molecular Association, and the Effect of Acids and Bases on Interfacial Tension. William D. Harkins, Earl C. H. Davies, and George L. Clark (*J. Amer. Chem. Soc.*, 1917, **39**, 541—596. Compare preceding abstract).—A continuation of the work of the previous paper (*loc. cit.*). The paper is chiefly theoretical, but a number of experiments are described on the measurement of the surface tension of sodium oleate and magnesium oleate solutions and their interfacial tensions towards benzene at 20°. It is shown that the molecules of liquids seem to be oriented, and in such a way that the least active or polar groups are oriented toward the vapour phase. The general law for surfaces is: If the structure of the surface of a liquid is supposed to be at first the same as that of the interior of the liquid, then the actual surface is always formed by the orientation of the least active portion of the molecule toward the vapour phase, and at any surface or interface the change which occurs is such as to make the transition to the adjacent phase less abrupt. This last statement expresses a general law, of which the adsorption law is only a special case. If the molecules are monatomic and symmetrical, then the orientation will consist of a displacement of the electromagnetic fields of the atoms. This molecular orientation sets up what is commonly called "the double electrical layer" at the surface of liquids and solids. On applying this law to a few special cases, the following orientations are deduced for several pure liquids: In water the hydrogen atoms turn toward the vapour phase and the oxygen toward the liquid. With organic paraffin derivatives, the CH_3 groups turn outward, and the more active groups, such as NO_2, CN, CO·OH, CO·OM, CO·OR, NH_2, $NH·CH_3$, NCS, COR, CHO, I, OH, or groups which contain N, S, O, I, or double bonds, turn toward the interior of the liquid. If any of these organic compounds are dissolved in water, their orientation on the water surface is the same as given above, with the active groups inward. The behaviour of these various groups is tabulated in the paper. At interfaces between two pure liquids the molecules turn so that their like parts come together in conformity with the general law. With solutions, the solute molecules orient so that the ends of the molecules toward the liquid *A* are as much like *A* as possible, and the ends toward *B* are as much like *B* as possible. So at interfaces between organic liquids and water, for example, the organic radicle sets toward the organic liquid, and the polar group toward the water.

If at an interface the transition from a liquid *A* to the liquid *B* is made by a saturated film of solute molecules, which may be termed *A*—*B*, that is, they have one end like *A* and the other like *B*, then the free surface energy is greatly reduced. For example, with water and benzene with sodium oleate as the solute, the free energy falls as low as 2 ergs/cm.^{2}. If the solvent is polar, such as water, then solutes will in general be positively adsorbed in the surface if they are less polar than water, and the least polar end of the molecule will be turned outward. Solutes more polar than water are negatively absorbed. Contrary to previous work, the present results show that bases do not lower markedly the interfacial tension between benzene and water. This is an important fact on account of its physiological applications. The important energy functions at surfaces are the total surface energy (μ or E_s), the free surface energy (γ), the latent heat of the surface (b), and the specific heat of the surface (c) all being for unit area. The total surface energy is independent of the temperature so long as $d\gamma/dT$ is constant, and is more characteristic of chemical constitution than the other functions. It is shown that the Eötvös–Ramsay–Shields method for the calculation of molecular association is of little value. A very extensive table of 336 liquids has been compiled in which values of E_s, γ, $d\gamma/dT$, and $(d\gamma/dT)/\gamma_0$ are given. The relationships of these data to the orientation are given in the other table already mentioned. A discussion is entered into on (i) the substitution products of the paraffins, (ii) the substitution products of benzene, and (iii) the orientation of the substitution products of benzene.

Films of solutes positively adsorbed at either liquid–vapour surfaces or liquid–liquid interfaces frequently become saturated. The rapidity with which saturation occurs depends on the nature of the solute, and increases with the length of the insoluble end of the molecule. Thus sodium oleate in water is very highly adsorbed, and the surface tension of the solution decreases with extreme rapidity. After the concentration of the solution reaches the value 0·002*N*, the surface tension no longer decreases, but remains constant up to 0·1*N* or more, which proves that the film has become saturated. The stability of the emulsoid particles seems to be brought about by orientation of molecules at the interface with the dispersion medium. The best emulsifying agents, for example, have very long molecules, with a polar or active group at one end of the molecule. For the emulsoid particle to be stable, the molecules which make the transition from the interior of the drop to the dispersion medium, or the molecules of the film, should fit the curvature of the drop. From this point of view the surface tension of very small drops is a function of the curvature of the surface. J. F. S.

Freezing of Water Absorbed in Lampblack. H. W. Foote and Blair Saxton (*J. Amer. Chem. Soc.*, 1917, **39**, 627—630. Compare A., 1916, ii, 230).—A continuation and confirmation of previous work. Lampblack containing absorbed water has been subjected to temperatures down to −78° in a dilatometer, and curves plotted of the temperature and dilatometer readings; heating curves were also obtained. The experiments show that the density of water which has been absorbed or adsorbed by lampblack is essentially the same as that of other water at the same temperature, although the last of the water did not freeze until the temperature was below −35°. The "apparent capillary water" in these experiments amounts to three-quarters of the weight of the carbon. The curves obtained in the present work differ only in one respect from those obtained from hydrogels. In hydrogels, the heating curves take on a decided curvature at as low a temperature as −20°, showing that the ice begins to melt at this temperature, whereas in the present case the curve is a straight line right up to zero, which shows that ice once formed, at no matter what temperature, does not melt again until the temperature is very near to zero. J. F. S.

Adsorption of Chromium Oxide by Hide Powder. A. W. Davison (*J. Physical Chem.*, 1917, **21**, 190—197).—The quantity of chromic oxide absorbed by standard hide powder has been determined in a series of experiments in which the only variable factor was the strength of the chrome tanning solution, which was made up by mixing a solution containing 120 grams of chrome alum in 1000 c.c. of water with a solution containing 30 grams of sodium carbonate in 100 c.c. of water.

Two grams of the hide powder were shaken for an hour with 250 c.c. of a solution containing 10 grams of sodium chloride per litre to ensure complete soaking of the powder. A measured volume of the tanning solution, made up to 25 c.c. by the addition of water, was then added to the flask containing the hide powder, and the shaking continued for four hours.

In order to estimate the absorbed chromic oxide, the contents of the flask were filtered, and the liquid adhering to the chromed hide powder removed as completely as possible by centrifugal action. The powder was then acted on with a little nitric acid and the dry residue heated in an electric furnace at a dull red heat. The sodium chloride and potassium sulphate in the ignited residue were removed by washing, and the residue, after correction for the ash of the hide powder, was taken as representing the chromic oxide absorbed.

If the quantity of the chromic oxide absorbed by 2 grams of hide powder is plotted against the concentration of the chromium in the residual solution, a continuous curve is obtained, the form of which corresponds with the ordinary adsorption formula. The results are therefore considered to support the view that the initial step in the process of chrome tanning consists in the adsorption of chromic oxide. H. M. D.

Selective Adsorption and Differential Diffusion. JEROME ALEXANDER (*J. Amer. Chem. Soc.*, 1917, **39**, 84—88).—A paper in which several qualitative experiments are described to show the different rates of diffusion of substances through colloids. This is followed by a discussion on the effects of differential diffusion and selective adsorption in connexion with the action of antitoxins on toxins, and with root formation and shoot formation in plants. J. F. S.

Inconstancy of the Solubility Product. II. ARTHUR E. HILL (*J. Amer. Chem. Soc.*, 1917, **39**, 218—231. Compare A., 1910, ii, 936).—Measurements have been made at 25° of the solubility of silver bromate, thallous chloride, and lead chloride in aqueous solutions containing varying amounts of acetic acid, and also of the solubility of tetramethylammonium iodide in solutions of potassium hydroxide and ammonium hydroxide. In four out of five cases the solubility decreases regularly with increasing quantity of the soluble electrolyte, but with lead chloride there is at first a slight increase followed by a very marked decrease. These results indicate that the ionic solubility product decreases with increase in the concentration of the soluble electrolyte. The proof of this is furnished by a consideration of the equilibrium in the solution which is saturated with respect to AB. As a consequence of double decomposition, the solution contains AB, CD, AD, and CB, and the four component ions. If the ion concentration is represented by capital and the concentration of the non-ionised molecules by small letters, then the total solubility, m, of AB may be expressed by $m=A+a+c$ and $m=B+a+d$. Multiplying these equations and extracting the square root gives $m=\sqrt{AB}+X$, in which X has a positive value. From this, it follows that, if m becomes less than $\sqrt{A\cdot B}$, the ionic solubility product must have a value which is smaller than that for a saturated solution of AB in pure water. The data obtained in the above measurements show that this condition is attained in four out of five cases, the exception being the solution of tetramethylammonium iodide in aqueous ammonia. H. M. D.

Solubilities of Several Substances in Mixed Non-aqueous Solvents. II. J. W. Marden and Mary V. Dover (*J. Amer. Chem. Soc.*, 1917, **39**, 1—7. Compare A., 1916, ii, 418).—The authors have determined the solubility at 25° of lithium chloride in mixtures of acetone and benzene, and of ethyl acetate and benzene; of mercuric chloride in mixtures of ethyl ether and chloroform, acetone and benzene, and ethyl acetate and benzene; and of salicylic acid in mixtures of acetone and benzene and ethyl acetate and benzene. Solubility determinations of the same substances at the same temperature have also been made in the pure solvents. It is shown that of the sixteen cases examined in the present and the preceding paper, five yield curves which present breaks, whilst the other eleven yield smooth solubility–composition curves. Of these eleven, in six cases the solubility was reduced by any given change in the percentage composition of the solvent by a constant fraction of the total difference between the solubility in the solution in question and in the poorer solvent. This is expressed by the equation $(C_1-C_2)/C_1=(C_2-C_3)/C_2=K$. In the five remaining cases, the relationship is expressed by the equation $(C_1-C_2)/\sqrt{C_1}=(C_2-C_3)/\sqrt{C_2}=K$. J. F. S.

The Formation of Salt Crystals from a Hot Saturated Solution. E. Tatum Long (*Amer. J. Sci.*, 1917, [iv], **43**, 289—292).—A description of an experiment, with photographs of the apparatus used, designed to show that crystals during development exert a lateral pressure sufficient to permit continued growth even against opposing external forces. In the experiment described, a hot saturated solution of common salt, under a small hydrostatic pressure, is forced into a closed rubber tube in which crystals grow and eventually burst the rubber. E. H. R.

The Constitution of Mixed Crystals. L. Vegard and H. Schjelderup (*Physikal. Zeitsch.*, 1917, **18**, 93—96).—To decide whether mixed crystals of isomorphous substances consist simply of superimposed layers of the two components or of a more intimate interpenetration, mixed crystals of potassium chloride and potassium bromide, and of potassium and ammonium bromides, in varying proportions have been examined by means of *X*-rays. The reflection method of Bragg was used, and it was found that the reflection maxima from cube and dodecahedron faces in the case of the mixed crystals were always normal in character and fell between those of the two components. Were the mixed crystals formed of alternating layers of the two components, it was to be expected that double maxima would be detected corresponding with the two reflection spectra from the components.

It is concluded that in mixed crystals of, for example, potassium chloride and bromide there is a space lattice similar to that of either component, some of the halogen atoms of the one kind being replaced by those of the other kind. The molecular volumes of the components undergo modification, that of the chloride being increased, that of the bromide diminished. If, in a 50% mixture of the two salts, the halogen atoms of the two kinds alternate regularly in the structure, it is to be expected that a new reflection maximum would be observed from the octahedron face (111) owing to the doubling of the lattice constant in the direction perpendicular to this face. Such a maximum could not, however, be detected, owing either to its necessarily feeble character or to the fact that the distribution of the halogen atoms of the two kinds is not of such a symmetrical character as to produce it. E. H. R.

X-Ray Analysis and Topic Axes of the Alkali Sulphates and their Bearing on the Theory of Valency Volumes. A. E. H. TUTTON (*Proc. Roy. Soc.*, 1917, [*A*], **93**, 72—89).—This paper is devoted to an attack on the Barlow-Pope theory of the relation between atomic volume and valency in crystals. The isomorphism of ammonium salts with corresponding salts of the alkali metals potassium, rubidium, and cæsium is discussed, in particular the close approach to equality between the structural dimensions of crystals of corresponding ammonium and rubidium salts. On account of their similar molecular volumes, isomorphous ammonium and rubidium salts readily form mixed crystals. Crystals of the sulphates have now been subjected to *X*-ray examination by Ogg and Hopwood (compare *Phil. Mag.*, 1916, [vi], **32**, 518), and the results fully confirm the close structural similarity of the ammonium and rubidium salts. The structural unit of the rhombic crystal contains in each case 4 molecules, as had been previously suggested by the author. The structures of these salts are held to be inconsistent with the valency volume theory, which gives to $(NH_4)_2SO_4$ a volume=24 and to Rb_2SO_4 a volume=12, whereas the actual volumes of the space units of the crystals are very nearly equal. E. H. R.

Protective Colloids. VIII. Tubera Salep as Protective Colloid. I. General Colloido-chemical Investigation of Salep Extract. A. GUTBIER and NORA KRÄUTLE (*Kolloid Zeitsch.*, 1917, **20**, 83—101. Compare this vol., ii, 168, 169).—An account is given of the preparation of colloidal extracts of tubera salep and of observations on the stability of these colloidal solutions, with special reference to the influence of concentration, temperature, and added electrolytes.

The data obtained in measurements of the viscosity of solutions of varying concentration are discussed in reference to Hatschek's theory that water is adsorbed by the colloidal particles, and it is calculated that 1 gram of the colloid combines with about 27 grams of water. In an electric field the colloidal particles move towards the cathode.

Observations made with dialysed and undialysed extract show considerable differences in regard to the influence of the several factors which have been examined. H. M. D.

Antagonistic Electrolytes and Jelly Formation. G. H. A. Clowes (*Proc. Amer. Soc. Biol. Chem.*, 1916, viii—ix; *J. Biol. Chem.*, 1917, **29**. Compare A., 1916, i, 583).—When sodium chloride is added in increasing proportion to aqueous suspensions of soaps or lipoids, the dispersion of the particles in water is at first promoted and reaches an optimum at approximately 0·15*M*-sodium chloride, which corresponds closely with the concentration of this substance in the blood. Subsequently, an aggregating effect is exerted, precipitation occurring at a concentration of 0·35 to 0·4*M*-sodium chloride, which appears to be the limiting concentration for the maintenance of life of marine organisms, of mice on intravenous injection, and the precipitation point for emulsions, jellies, and a variety of other physical systems.

Koch's curve (A., **1907**, i, 573) showing the amount of calcium chloride required to precipitate lecithin at different concentrations of sodium chloride corresponds closely with curves obtained by the drop method (Clowes, *loc. cit.*) when sodium chloride is added in increasing proportion to an aqueous phase containing a constant amount of soap passed through neutral oil. The similarity in these antagonistic curves of calcium chloride and sodium chloride and other salts having a more readily adsorbed anion in such widely diversified systems as living protoplasm, the blood-clot emulsions, soap jellies and films, and soap and lipoid suspensions, and the existence of the common limiting concentrations at which individual salts like sodium chloride and calcium chloride produce inhibiting effects in all these systems, suggest the probability that protoplasmic equilibrium and the formation of reversible protoplasmic jellies are dependent on what the author designates as an imperfect reversal of phase relations promoted by the action of antagonistic electrolytes on interfacial films of soap and lipoid, just as in reversal of equilibrium in the case of emulsions of oil and water. H. W. B.

Plasticity. Emil Podszus (*Kolloid Zeitsch.*, 1917, **20**, 65—73). —A discussion of the factors which determine the plasticity which is characteristic of mixtures of clay and water in their application in the ceramic industries. The author adopts the view that the coagulation of substances in sol form is an essential feature of such systems, and it is shown that many substances, other than clays, may be transformed into sols with plastic qualities which are quite similar to those familiarly associated with the clays. H. M. D.

The Laws of Swelling. I. The Swelling in Water without Complications. J. R. Katz (*Koll. Chem. Beiheft*, 1917, **9**, 1—182).—The phenomena associated with the swelling of substances in contact with water have been subjected to examination in experiments with a number of different substances, in the choice of which the principal consideration was the avoidance of all possible disturbing factors. The conditions requisite for the attainment of this end are satisfied only by definite chemical compounds which are non-porous, do not combine with the absorbed liquid, and are characterised by the absence of irreversible changes. These conditions are fulfilled by amorphous and crystalline substances, and both types have been examined.

The observations indicate the nature of the dependence of the vapour pressure, the heat of swelling, the change in volume, and the specific heat on the degree of swelling, defined as the ratio between the weight of the absorbed water and that of the dry substance under examination. The results for different substances show that the chemical nature of the substance is without influence on the general character of the phenomena associated with the swelling process.

For all the amorphous substances examined, the curve showing the relation between the vapour pressure (expressed in terms of that of pure water at the same temperature) and the degree of swelling (i) is of the same type. For small values of i, the curve runs nearly horizontal; the curve then rises, being at first convex and later concave towards the i axis, the last portion being again nearly horizontal.

The heat developed in the absorption of i grams of water by 1 gram of the dry substance is satisfactorily represented by the formula $W = Ai/(B+i)$, in which A and B are constants characteristic of the swelling substance. The corresponding contraction in volume may be expressed by a formula of the same type. These two quantities are, in fact, approximately proportional, and the ratio for different substances is of the same order of magnitude.

The decrease in the free energy and the heat development associated with the swelling process are approximately equal, and from this it follows that nearly the whole of the energy of swelling may be transformed into external work.

In the case of crystalline substances, the only measurements made were those relating to the vapour pressure. These show that the dependence of the relative vapour pressure on the degree of swelling is essentially the same as for amorphous substances.

Not only do the most various substances behave similarly in regard to the swelling processes, but it is further shown that there is a close resemblance in the relative vapour pressure, the heat of swelling, and the volume curves for mixtures of non-volatile liquids, such as sulphuric acid, phosphoric acid, and glycerol, with water. The ratio of the heat development to the volume contraction is of the same order for both groups.

This close similarity in the phenomena associated with the swelling of substances in water and in the changes which accompany the formation of binary liquid mixtures leads to the conclusion that the swelling process is to be regarded as the formation of a solid solution of water in the swelling substance. This idea is obviously incompatible with the micellary hypothesis put forward by Nägeli to explain the behaviour of swelling substances. It disposes of the necessity for the assumption of complex structural units and replaces these by the simpler molecules. The systems which result from the swelling of substances when brought into contact with suitable liquids are accordingly to be looked on as ideal concentrated solutions. H. M. D.

Non-, Uni-, and Bi-variant Equilibria. XIII. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 867—880. Compare this vol., ii, 169, 195).—A further theoretical discussion of the equilibrium relations in ternary systems with two indifferent phases. H. M. D.

Heterogeneous Equilibria between Aqueous and Metallic Solutions. III. The Interaction of Mixed Salt Solutions and Liquid Amalgams. A Study of the Ionisation Relations of Sodium and Potassium Chlorides and Sulphates in Mixtures. G. McP. Smith and T. R. Ball (*J. Amer. Chem. Soc.*, 1917, **39**, 179—218. Compare A., 1913, ii, 124).—The behaviour of solutions containing sodium and potassium salts towards sodium potassium amalgams has been examined with a view to the elucidation of the ionisation of salts in mixtures. The equilibrium in this system corresponds with $KHg_m + Na^{\cdot} \rightleftharpoons NaHg_n + K^{\cdot}$, and by application of the law of mass action, the relation

$$[KHg_m][Na^{\cdot}]/[NaHg_n][K^{\cdot}] = C_0$$

is obtained, in which C_0 represents the constant for infinite dilution. For solutions in which the ionisation is incomplete, the equilibrium constant may be written

$$[KHg_m][NaX]_c/[NaHg_n][KX]_c = C_c,$$

where the suffix c refers to the total salt concentration. By investigation of the connexion between the value of C_c for the salt concentration c and the value C_0 corresponding with complete ionisation, it is possible to obtain information relating to the ionisation of sodium and potassium salts in their mixtures.

According to experiments with equivalent mixtures of sodium and potassium chlorides up to 4·0*N*-concentration, the value of C_c at 25° decreases linearly with increasing concentration of the solution. For equivalent mixtures of sodium and potassium sulphates at concentrations varying from 0·2 to 2*N*, the value of C_c is nearly independent of the total salt concentration. The data for equivalent mixtures of sodium sulphate and potassium chloride up to a concentration of 3·0*N* show, on the other hand, that C_c decreases with increasing concentration, but the decrease is not linear. The results obtained with equivalent mixtures of sodium and potassium chlorides at temperatures between 15° and 30° show that C_c decreases with rising temperature. From these results it has been possible to derive the heat change accompanying the reaction $KHg_m + NaCl = NaHg_n + KCl + (m-n)Hg$, the value found being -3000 cal.

The interpretation of the results leads to the view that complex molecules, $NaKCl_2$, are formed in the chloride solutions, and the mixed sulphate, $NaKSO_4$, in the sulphate solutions. H. M. D.

The Course of Crystallisation in Ternary Systems of Chlorides of Univalent and Bivalent Metals. TH. LIEBISCH (*Zeitsch. anorg. Chem.*, 1917, **99**, 50—66).—The ten ternary systems of chlorides of univalent and bivalent metals which have so far been investigated are theoretically reviewed, with special reference to the case in which the crystalline phases include the components *A*, *B*, and *C*, and also a binary compound with incongruent melting point, the method used being that of constructing a crystallisation path on the projection of the liquidus surface.

C. H. D.

Normal and Acid Sodium Sulphates. PAUL PASCAL (*Compt. rend.*, 1917, **164**, 628—630).—A study of the equilibrium of the ternary system H_2SO_4–Na_2SO_4–H_2O between the temperature limits −45° and 210°. The results are set out as a trilinear projection of the isotherms of the surface of equilibrium of the solid and liquid phases. The diagram, coupled with a study of the cooling of the ternary mixtures, indicates that with the acid sulphates, from the manufacture of nitric acid, where the acidity is above 40·81%, solidification occurs below 184°, giving at first crystals of sodium hydrogen sulphate, until at 105° the remaining liquid solidifies to the acid salt, $NaHSO_4,H_2SO_4$. Solutions of sodium hydrogen sulphate, about 75% in strength, saturated at about 100°, give after crystallisation a residual liquid containing about 45% of sulphuric acid and only about 10% of the normal sulphate.

W. G.

A Chemical Method of Determining the Strength of Sparingly Soluble Inorganic Bases. K. A. VESTERBERG (*Zeitsch. anorg. Chem.*, 1917, **99**, 11—21).—The strength of sparingly soluble inorganic bases has usually been determined by measuring the hydrolysis of the sulphates, nitrates, or chlorides. The numbers differ very little for different bases, and better results are obtained by using the acetates and measuring the hydrolysis by the extraction method. The error caused by the disturbance of the equilibrium by removal of acetic acid by the solvent is overcome by agitating the ether solution with successive fresh quantities of the aqueous acetate solution. After three to five extractions, the ether solution is in equilibrium with unaltered acetate solution.

The ethyl ether is freed from the acid usually present in commercial samples by keeping over concentrated sodium hydroxide solution and washing with water, free from carbon dioxide, just before use. The acetate solutions are prepared from purified salts or by the addition of pure sodium acetate to the solution of the sulphate, the concentration being made 9 to 10% greater than is required to allow for the increase of volume on shaking with ether. Water free from carbon dioxide must be used. The titrations are mostly performed with 0·025*N*-barium hydroxide, with phenolphthalein as indicator. The metal in the aqueous solution must be estimated after the extraction.

C. H. D.

Propagation of Flame in Mixtures of Acetone and Air. RICHARD VERNON WHEELER and ARNOLD WHITAKER (T., 1917, **111**, 267—272).—This paper gives the results of the first of a series of investigations designed to throw light on the conditions under which the vapours of inflammable liquids used in industry form dangerously explosive mixtures with air.

The higher and lower limits of inflammability have been determined for horizontal, downward, and upward propagation of flame in tubes 2·5, 5, and 10 cm. diameter. Above 5 c.c. the diameter of the tube has little influence on the limits, and the results indicate that for large pipes the lower and upper limiting mixtures correspond respectively with about 2 and 10% of acetone vapour.

The graph obtained by plotting the speed of propagation of flame ("uniform movement") in a 2·5 cm. tube against the percentage of acetone vapour shows that the speed has its maximum value for a mixture containing 5·5% acetone. This speed is about 96 cm. per sec., and for pipes of 30, 60, and 90 cm. diameter may be expected to be respectively 2·5, 3, and 3·5 times as great.

H. M. D.

Chemical Reactions in Anisotropic Liquids. III. THE. SVEDBERG (*Kolloid Zeitsch.*, 1917, **20**, 73—76).—According to previous observations (A., 1916, ii, 306, 383), the rate of change with time of the electrical conductivity of a solution of picric acid in *p*-azoxyphenetole increases with the temperature, and changes abruptly at the clearing point of the solvent. Further experiments show that a similar effect is obtained when the anisotropy is destroyed by the addition of foreign substances, such as diphenyl and naphthalene.

The fact that the initial rate of increase of the conductivity of pure *p*-azoxyphenetole is very nearly the same as that of a solution of picric acid in this solvent, leads to the conclusion that the increase in conducting power is to be attributed to decomposition of the *p*-azoxyphenetole, and not, as previously supposed, to the decomposition of the picric acid.

H. M. D.

Decomposition of Chloro- and Bromo-acetic Acids in Alcoholic Solution. HENRY W. CASSEL (*Zeitsch. physikal. Chem.*, 1917, **92**, 113—126).—The investigation of the rate of hydrolysis of chloro- and bromo-acetic acids in aqueous alcoholic solutions at 70° has shown that the velocity of the reaction diminishes in proportion to the alcohol content of the solvent. The reaction proceeds in accordance with the equation for a unimolecular change.

When the reaction mixture contained in a quartz vessel is exposed to the light emitted by an arc lamp, the reaction proceeds differently, in that acetaldehyde is produced in accordance with the equation $CH_2X{\cdot}CO_2H + C_2H_5{\cdot}OH = CH_3{\cdot}CO_2H + CH_3{\cdot}COH + HX$, in which X represents chlorine or bromine. Experiments at 18° in which the influence of the alcohol concentration was examined, show that in the case of bromoacetic acid the velocity of the reaction increases considerably with the proportion of alcohol in the solvent, attains a maximum in 50% solution, and decreases when the alcohol content is further increased. The changes in the velocity are much smaller in the case of chloroacetic acid, and the velocity remains the same when the alcohol concentration increases from 50 to 100%. Under comparable conditions as regards the solvent, bromoacetic acid is decomposed more rapidly than chloroacetic acid, whether the reaction takes place in the dark or under the influence of light. The active rays are of wave-length less than 250 $\mu\mu$. H. M. D.

Consecutive Reactions. II. Kinetics of the Hydrolysis of the Methyl Esters of Oxalic Acid. ANTON SKRABAL (*Monatsh.*, 1917, **38**, 29—52. Compare A., 1916, ii, 477).—The rate of hydrolysis of methyl oxalate and of potassium methyl oxalate, both by acid and alkali, has been determined for a series of concentrations at 25°. The hydrolysis of the normal ester takes place in two stages, which have such different velocities that the calculation of the velocities by the method used for single-stage reactions can be effected. In alkali hydroxide solutions the rate of hydrolysis of the ester acid is still measurable, whilst that of the normal ester to the first stage is unmeasurably fast. The measurements were therefore carried out with a mixture of ammonia and ammonium chloride, the alkalinity of which is of about the same dimensions as the esters. The ratio of the velocity constants was found to be of the order 10,000:1. In the case of acid hydrolysis, the velocity was of the normal order and the measurements were carried out in the usual way with hydrochloric acid. In this case the ratio of the velocity constants is 2:1. The actual constants obtained are: first stage—alkaline hydrolysis, $k_1 = 10^6$; acid hydrolysis, $k_1 = 0{\cdot}0116$; second stage—alkaline hydrolysis, $k_2 = 10^2$; acid hydrolysis, $k_2 = 0{\cdot}0058$. J. F. S.

Reactions with Halogen-substituted Acids. II. Action of Sodium Methoxide on Monobromosuccinic Acid, α-Bromo*iso*butyric Acid, β-Bromobutyric Acid, and α-Bromopropionic Acid. E. HÖST MADSEN (*Zeitsch. physikal. Chem.*, 1917, **92**, 98—112. Compare A., 1914, ii, 260).—The interaction between sodium methoxide and the sodium salts of various halogen-substituted acids in methyl-alcoholic solution has been examined by measurements of the alkalinity and the bromide concentration after various intervals of time.

The results indicate that intermediate products are formed in the case of bromosuccinic and β-bromobutyric acids, in that the increase in the bromide concentration takes place more rapidly than the decrease in the alkali titre. These intermediate substances appear to be formed at the same rate in anhydrous methyl alcohol and in methyl alcohol which contains three gram-molecules of water per litre, but the rate of decomposition of the intermediate compounds is greater in presence of water. The formation of intermediate products appears to be characteristic of the β-substituted acids, for the experiments with α-substituted acids gave no evidence of this phenomenon.

The kinetic data are discussed in reference to the order of the several reactions investigated. H. M. D.

Reactions of both the Ions and the Molecules of Acids, Bases, and Salts. The Inversion of Menthone by Sodium, Potassium, and Lithium Ethoxides. W. A. Gruse and S. F. Acree (*J. Amer. Chem. Soc.*, 1917, **39**, 376—388).—The authors have measured the velocity of inversion of *l*-menthone in absolute alcohol solution by the ethoxides of sodium, potassium, and lithium. The measurements were carried out in 70 cm. polarimeter tubes by means of a Schmidt and Haensch polarimeter, capable of reading to 1/1000°. The rotation measurements were made with the mercury-green line 546·1, obtained from a mercury vapour lamp, using a mercury-green line Wratten filter. The reactions took place in a thermostat at 25°, which did not vary more than 0·005°. Dilute solutions varying from $N/32$ to $N/512$ were used. By substituting the molecular velocity constants K_N and the corresponding α values in the proper equations, values have been obtained for the catalytic activity of the ethoxide ion and the non-ionised molecule of the metallic ethoxide. The constants expressing the activity of the ethoxide ion have been found to be the same, whether the experiment be made with sodium, potassium, or lithium ethoxide, namely, $K_i=0·501$, $K_i=0·501$, and $K_i=0·496$ respectively. The constants K_m, expressing the activity of the non-ionised molecule of the metallic ethoxide, have been found to be very close for sodium and potassium ethoxides, namely, $K_m=0·693$ and 0·701 respectively, but somewhat smaller for lithium ethoxide, $K_m=0·478$, which is practically the same as that found for the ethoxide ion, $K_i=0·496$ in the case of lithium ethoxide. Making use of the above considerations, satisfactory explanations have been offered for the approximate equality of the velocity constants, K_N, found for sodium and potassium ethoxides, as well as for the deviation of the lithium ethoxide from this value; for the fact that the molecular velocity constant, K_N, for lithium ethoxide remains unchanged with dilution, whilst the same values for sodium and potassium ethoxides decrease considerably as the concentration decreases, and for the nearly identical value assumed by the velocity constants for all three ethoxides in very dilute solutions. The average values of the constants for the ionic and molecular activities have been substituted in the equation

$$K_N=K_i\alpha+K_m(1-\alpha),$$

and the calculated values of K_N have been compared with the experimental values. The average deviation is about 1·5%.

J. F. S.

Kinetics of Furfuraldehyde Formation from Pentoses (Arabinose). Robert Kremann and Hermann Klein (*Monatsh.*, 1917, **38**, 63—75).—The authors have studied the kinetics of the formation of furfuraldehyde from arabinose by the action of sulphuric acid and hydrochloric acid. Five c.c. of 1·054N-arabinose solution were mixed with 10 c.c. of 4·7N-sulphuric acid, 2·35N-sulphuric acid, 0·470*N*-sulphuric acid, and 4·43*N*-hydrochloric acid respectively. The flasks containing the various mixtures were sealed and heated in a thermostat at 95° for measured times. They were then withdrawn, allowed to cool for fifteen minutes, and opened. The contents were neutralised with sodium hydroxide and the furfuraldehyde distilled off, converted into furfuraldehyde semioxamazide, and weighed as such. The results are expressed in dx/dt curves, where dx represents the amount of furfuraldehyde semioxamazide formed at the time dt. The results fall on to two different curves, the one being an S-shaped curve, the other a slowly rising curve. There is no apparent reason why the results should fall on one curve rather than on the other. The author concludes that at 95° a high concentration of hydrogen ions can produce in arabinose solutions, in the course of the reaction, either a positive catalyst *A*, which accelerates the furfuraldehyde formation autocatalytically, or a catalyst *B*, which accelerates the subsidiary reaction, so that in the latter case only one-third of the quantity of the furfuraldehyde expected appears to be formed. With decreasing acid concentration the two curves come closer together, and eventually coincide to represent a reaction of the first order. The S-shaped curve is represented by the equation $dx/dt=(k_1+k_2x)(a-x)$, that is, by the typical equation for an auto-catalytic reaction. J. F. S.

Kinetics of Invertase Action. J. M. Nelson and W. C. Vosburgh (*J. Amer. Chem. Soc.*, 1917, **39**, 790—811).—A comprehensive study of the kinetics of invertase action, the data obtained showing that (1) the velocity of inversion is directly proportional to the concentration of the invertase, (2) that the velocity is nearly independent of the concentration of the sucrose in the more concentrated sugar solutions, whilst in very dilute solutions the velocity increases with the increase in concentration of the sugar up to a maximum, (3) the velocity-coefficient increases as the inversion proceeds, (4) the results agree with the heterogeneous reaction view (compare Henri, A., 1906, ii, 13; Nelson and Griffin, A., 1916, i, 516), and contradict the view that the kinetics of invertase action conform to the unimolecular law for homogeneous reactions (compare Hudson, A., 1908, i, 605, 856). Adsorption appears to be one of the controlling factors in the kinetics of invertase action, and the curve for the velocity of inversion, the concentrations of the sucrose being taken as abscissæ, has the same general shape as adsorption curves (compare Henri, *loc. cit.*). The inversion is of a type similar to, but more complicated than, the heterogeneous catalytic reaction of the dissociation of stibine into antimony and hydrogen in the presence of antimony (compare Stock and Bodenstein, A., 1907, ii, 181). A peculiar phenomenon with regard to the dilution of invertase solution was noticed, namely, that invertase solutions could be diluted in the presence of a small amount of acid without changing their relative activity, but, if the acid was omitted, solutions of widely differing activity were obtained. W. G.

The Catalytic Influence of Acids in Lactone Formation. I. Valerolactone. Hugh Stott Taylor and Harold Wilberforce Close (*J. Amer. Chem. Soc.*, 1917, **39**, 422—435. Compare Henry, A., 1892, 1303).—A study of the catalytic action of hydrochloric acid and chloroacetic acid on the conversion of γ-hydroxyvaleric acid into valerolactone. The acid was prepared from the lactone as required either by the action of barium hydroxide, the barium being subsequently precipitated with the calculated quantity of $N/4$-sulphuric acid, or by the action of a suspension of lead hydroxide, the lead being afterwards precipitated with hydrogen sulphide. The values obtained with the acid prepared by the second method were consistently higher by about 3% than with the acid prepared by the first method, and at present this discrepancy cannot be explained. The conversion took place at 25° in the presence of varying concentrations of hydrochloric or chloroacetic acid, in the presence or absence of varying concentrations of the corresponding potassium salt. In the case of hydrochloric acid it is shown that the catalytic influence is not strictly proportional to the hydrogen-ion concentration as determined by conductivity measurements. The presence of potassium chloride increases the catalytic effect of hydrochloric acid. The catalytic effect can be expressed in terms of a catalytic activity of hydrogen-ion and undissociated molecule, but the ratio of these two effects is different if calculated from a series of acid concentrations or from a series of constant acid and varying neutral salt concentrations (compare Dawson and Reiman, T., 1915, **107**, 1426). The catalytic ratio in the case of hydrochloric acid is of the same magnitude as that observed in ester catalysis (compare Taylor, A., 1915, ii, 248).

The results obtained with chloroacetic acid as a catalyst show certain abnormalities, which cannot at present be satisfactorily explained. No concordant figures could be obtained from any pair of results for the catalytic ratio. W. G.

Numerical Relation of Atomic Weights to Atomic Numbers. Reginald Graham Durrant (*J. Amer. Chem. Soc.*, 1917, **39**, 621—626).—A theoretical paper in which the author discusses the work of Harkins and Wilson on the relationships existing between the atomic weights and atomic numbers of the elements (see Harkins and Wilson, A., 1915, ii, 544). Harkins and Wilson find that the relationship between atomic weight and atomic number is given, for the lighter elements, by the equation $W=2n+\{\frac{1}{2}+[(-1)^{n-1}\times\frac{1}{2}]\}$, but for the heavier elements another term has to be introduced, and the equation becomes

$$W=2(n+n')+[\tfrac{1}{2}+\tfrac{1}{2}(-1)^{n-1}].$$

The n' values are not given by the above-mentioned authors, and a table of these values is appended to the present paper. A graph of the n' values against the atomic numbers approximates on the whole to four straight lines: (1) a horizontal line along the axis from helium to chlorine; (2) a shorter horizontal line from titanium to cobalt ($n'=2$); (3) a long line from copper to bismuth inclined at an angle the tangent of which is $\frac{1}{3}$; and (4) a short line parallel to (3), but above it, from niton to uranium. The slope in the curves (3) and (4) can be reduced to the horizontal by obtaining the values $2[n+(n-29)/3]$; this is done in the paper, and the values $(W-2n)$ and $\{W-2[n+(n-29)/3]\}$ have been plotted against the atomic numbers. The deviations of the atomic weights from the doubled atomic numbers are considered.

J. F. S.

Twenty-fourth Annual Report of the Committee on Atomic Weights. Determinations Published During 1916. GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1917, **39**, 333—341).—A *résumé* of the atomic weight determinations of the year 1916, which includes the numerical details of determinations on hydrogen (Burt and Edgar, A., 1916, ii, 427), H=1·00769; argon (Schultze, A., 1915, ii, 833), A=39·945; zinc (Baxter and Grose, A., 1916, ii, 327), Zn=65·381; bromine (Moles, A., 1916, ii, 526), Br=79·926; yttrium (Hopkins and Balke, this vol., ii, 34), Yt=88·91; columbium (Smith and van Haagen, A., 1915, ii, 692), Cb=93·13; cadmium (Baxter, Grose, and Hartmann, A., 1916, ii, 327), Cd=112·407; tin (Baxter and Starkweather, A., 1916, ii, 637), Sn=118·703; neodymium (Baxter, Whitcomb, Stewart, and Chapin, A., 1916, ii, 325), Nd=144·261; dysprosium (Engle and Balke, this vol., ii, 259), Dy=164·228; radioactive lead (Richards and Wadsworth, this vol., ii, 91), Pb(Ra)=207·183—206·084; lead (Œchsner de Coninck and Gérard, this vol., ii, 33), Pb=206·98; bismuth (Œchsner de Coninck and Gérard, A., 1916, ii, 189), Bi=208·50.

J. F. S.

The Structure of Inorganic Compounds. SAMUEL HENRY CLIFFORD BRIGGS (T., 1917, **111**, 253—267).—The author has previously attempted (T., 1908, **93**, 1564) to devise formulæ for complex salts on the basis of the conception of duplex affinity, and a further study of this hypothesis has now been made from the point of view of the electron theory.

In addition to the distinction between positive and negative affinity, a further distinction is made between primary and secondary affinity. The secondary affinity only shows itself when the primary affinity has come into play. This is illustrated by reference to the ammoniacal copper compounds. The examination of these shows that cuprous compounds combine with a maximum of three molecules of ammonia and cupric compounds with six molecules, whilst metallic copper, that is to say, the neutral atom, is incapable of direct combination with ammonia. It would seem, therefore, that the copper atom develops negative (secondary) affinity when it has lost an electron, and when it has lost two electrons the negative affinity becomes more pronounced. Combination of atoms as a result of the saturation of primary affinity only is accompanied by a transfer of electrons from one atom to the other, whereas no such transfer takes place when the secondary affinities are saturated.

The theory is examined in reference to the constitution of ammonia and ammonium salts, the strengths of acids and bases, the stability of the compounds of ammonia with metallic salts, and the phenomenon of polymerisation. This leads to the view that compounds formed by the saturation of primary affinity only are of the "strong electrolyte" type, those formed by the saturation of secondary affinity only of the "molecular compound" type, and those formed by the saturation of both kinds of affinity of the "organic compound" or "paraffin" type. These three categories represent only extreme types, and most compounds are of intermediate character.

It is pointed out that the formulæ suggested on the above theory are purely affinity, and not valency formulæ. It may, indeed, be doubted whether a theory of valency is admissible in modern inorganic chemistry. H. M. D.

A Simple Gas Generator. R. O. FERNANDEZ (*J. Amer. Chem. Soc.*, 1917, **39**, 271).—A generator of the Kipp type constructed from apparatus available in every laboratory.

H. M. D.

An Efficient Desiccator. L. S. PRATT (*J. Amer. Chem. Soc.*, 1917, **39**, 271—272).—The apparatus consists of a Buchner funnel connected below through a stopcock and safety flask with a water-pump. Resting on the funnel is a heavy brass disk with a ring or sheet of rubber cemented on the lower surface, which affords an airtight joint when pressure is brought to bear on the disk by means of screws acting between the disk and a metal collar beneath the funnel. A brass tube passes through the centre of the disk, and this tube is connected through a stopcock to a system of drying towers. The material to be dried is placed in the funnel, the disk placed in position, and by means of the pump a current of dry air or inert gas is forced through the funnel. If the material requires to be dried at an elevated temperature, the apparatus may be enclosed in an air-bath. H. M. D.

Laboratory Experiment. Enrichment of Illuminating Gas. ROSS ALLEN BAKER (*J. Amer. Chem. Soc.*, 1917, **39**, 646).—A trap, consisting of a wide-mouthed bottle, is introduced between the gas outlet and a Bunsen burner. A copper wire is bound round one of the tubes which project through the stopper and serves to support a piece of calcium carbide. The Bunsen is lighted so that it is quite non-luminous, the carbide is then shaken into water, contained in the bottle, when the flame becomes luminous owing to the liberated acetylene. J. F. S.

Inorganic Chemistry.

Electrolytic Formation of Perchlorate. E. L. Mack (*J. Physical Chem.*, 1917, **21**, 238—264).—The mechanism of the formation of perchlorate by the electrolysis of chlorate solutions is usually regarded as that expressed by the equation $2ClO_3' + H_2O + 2F = HClO_4 + HClO_3$, a view first put forward by Oechsli (A., 1904, ii, 22). It is pointed out that this theory rests on several assumptions for which there is no experimental evidence, and that it does not account satisfactorily for the very marked decrease in the yield of perchlorate when platinised platinum anodes are substituted for smooth platinum anodes nor for the decrease in the efficiency with rising temperature. On the other hand, it is claimed that the phenomena associated with the electrolytic formation of perchlorate can be easily and satisfactorily explained on the assumption that the action consists in the combination of the chlorate ions with active oxygen resulting from the discharge of oxygen or hydroxyl ions at the anode. This view is supported by Schoch's experiments (A., 1911, ii, 14), which showed that in a $N/3$-solution of potassium chlorate with an iron anode, perchlorate formation begins when the anode potential reaches +0·023 volt, whereas oxygen is not evolved until the anode potential reaches +1·5 volts. It is thus clear that the electrolytic formation of perchlorate absorbs an amount of energy which is very much smaller than that required for the liberation of oxygen or the discharge of the chlorate ion.

In support of the author's theory, it has been found that chlorate may be oxidised to perchlorate by persulphuric acid, ozone, or hydrogen peroxide in acid solution. The oxidation may also be effected by the action of oxygen which has been activated by ultraviolet light. The reaction may be represented by the equation $HClO_3 + O = HClO_4$, and for a given concentration of chlorate the rate of oxidation will depend on the concentration of the active oxygen. The conditions obtaining in the experiments in which the chlorate has been oxidised to perchlorate by purely chemical agents are quite comparable with those attending electrolysis, and there are thus grounds for the assumption that the action is of the same kind. H. M. D.

Preparation of Sulphurous Acid. Edward Hart (*J. Amer. Chem. Soc.*, 1917, **39**, 376).—Fuming sulphuric acid containing 30% SO_3 is warmed with lump sulphur. The sulphur dissolves, forming a blue solution, from which, on warming, sulphur dioxide is given off mixed with some sulphur trioxide. Evolution of sulphur dioxide ceases when all the sulphur trioxide has been acted on and the sulphur melts. W. G.

The Synthesis of Ammonia. HENRY LE CHATELIER (*Compt. rend.*, 1917, **164**, 588—590).—Historical. The author claims priority over Haber for the synthesis of ammonia under pressure.

W. G.

The New Values of the Atomic Weights of Carbon and Sulphur in the International Table for 1916. E. MOLES (*J. Chim. Phys.*, 1917, **15**, 51—59).—Further evidence is brought in support of Guye's view (compare this vol., ii, 198) that the revisions of the atomic weights of carbon and sulphur proposed for 1916 by the International Committee are premature and not justified. Recalculating the values from the results of Richards and Hoover (compare A., 1915, ii, 96), based on the atomic weight of sodium, the author arrives at the results $C=11·996—12·001$ and $S=32·048—32·056$.

W. G.

The Faulty Values of the Atomic Weights of Carbon and Sulphur. PH. A. GUYE (*J. Chim. Phys.*, 1917, **15**, 60—63).—Further arguments in support of Moles's views (compare preceding abstract).

W. G.

Crystallographic Constants of some Artificial Crystals. HERM. ROSE (*Centr. Min.*, 1917, 85—87).—Cæsium dithionate, $Cs_2S_2O_6$, crystallises in the trapezohedral tetartohedral class of the hexagonal system [$a:c=1:0·6316$]. It is isomorphous with potassium and rubidium dithionates, the angular measurements being very close to those of the latter. Optically, the crystals are positively uniaxial and circularly polarising. For yellow light, $\omega=1·444$, $\epsilon=1·491$.

The hydrated salt, $2Cs_2S_2O_6,H_2O$, crystallises in the holohedral class of the rhombic system [$a:b:c=0·8832:1:0·5058$]. The optic axial plane is (010), the acute positive bisectrix $\perp$(010), $2E_{Na}=51·5°$, $\nu>\rho$. Measurable crystals of the corresponding rubidium salt were not obtained.

Terpin, $C_{10}H_{18}(OH)_2$, is rhombic holohedral [$a:b:c=0·7888:1:0·8224$]. There is a perfect cleavage parallel to (001). The optic axial plane is also parallel to (001), the axial angle in monobromonaphthalene for the green mercury line $\lambda=546·1\ \mu\mu$ being $2H=72°5'$. For the same line, $\alpha=1·5209$, $\beta=1·5292$, $\gamma=1·5416$, whence $2V=79°0'$. Calculated from $2H$ and β, $2V=79°42'$.

E. H. R.

The Oxy-salts of the Alkaline Earth Metal Haloids. Equilibria in Ternary Systems. I. J. MILIKAN (*Zeitsch. physikal. Chem.*, 1917, **92**, 59—80).—The basic salts formed by the alkaline earth metal haloids have been derived from a study of the equilibrium relations in the ternary system formed by the alkaline earth metal haloid, the corresponding hydroxide and water. The results obtained with calcium chloride and bromide and with barium chloride, bromide, and iodide have been previously described (A., 1912, ii, 760).

The data for calcium iodide at 25° show the existence of the basic salt, $CaI_2,3CaO,16H_2O$, which is stable in contact with solutions containing from 28·44 to 66·68% of calcium iodide. The only basic chloride of strontium has the composition $SrCl_2,SrO,9H_2O$, and this only exists in contact with solution at temperatures above 20·5°. Below this temperature the chloride, $SrCl_2,6H_2O$, and the hydroxide, $SrO,9H_2O$, may co-exist as solid phases in contact with aqueous solutions. The solution saturated with respect to these substances at 0° contains 0·31% of strontium oxide and 30·58% of strontium chloride.

Observations at 25° show that strontium bromide forms the basic salt $SrBr_2,SrO,9H_2O$. At this temperature it can only exist in contact with solutions containing from 40·66 to 49·79% of strontium bromide. Strontium iodide at 25° yields a basic salt of the composition $SrI_2,2SrO,9H_2O$, which is stable in contact with solutions containing from 49·37 to 64·04% of strontium iodide.

Incidentally, the cryohydratic temperatures for strontium bromide and barium bromide were determined. The former is at −28° and the eutectic solution contains 41·7% of strontium bromide. The cryohydratic temperature of the barium salt is at −22·6° and the eutectic solution contains 46·6% of barium bromide.

H. M. D.

Action of Magnesium on Aqueous Solutions. FREDERICK H. GETMAN (*J. Amer. Chem. Soc.*, 1917, **39**, 596—604. Compare this vol., ii, 90).—The action of 0·1*N*-potassium chloride has been examined on chemically pure magnesium prepared by distillation; it is shown that this solution acts just as readily on the pure magnesium as on the material previously used (*loc. cit.*), which contained 0·5% of impurity. The hydrogen-ion concentration was measured in cells of the type $Hg|Hg_2Cl_2,0{\cdot}1NKCl||0{\cdot}1NKCl|Pt\ H_2$, into which were placed pure magnesium and 99·5% magnesium as hydrogen generators; the hydrogen-ion concentrations were practically identical in the two cases, so that it seems safe to conclude that the impurity in the magnesium previously used did not seriously affect the results. The behaviour of magnesium (99·5%) in a series of 0·1*M*-solutions of twenty typical electrolytes was also examined in the same way as with potassium chloride, the volume of hydrogen liberated by a surface of 412 sq. cm. in twenty-four hours being measured. The general behaviour in these solutions was found to be much as in the case of potassium chloride. This is considered to be additional evidence in favour of the hypothesis already advanced that in the reaction represented by the equation $Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$ the solute acts catalytically. In solutions of salts which undergo hydrolysis, the evolution of hydrogen was found to be accelerated if the base of the salt was weak and retarded if the base of the salt was strong. Non-electrolytes appear to exert no appreciable influence on the rate of reaction. This suggests that the effective catalytic agency is ionic. J. F. S.

Cerium-Iron Alloys. Rudolf Vogel (*Zeitsch. anorg. Chem.*, 1917, **99**, 25—49).—The alloys are prepared in quantities of 20 grams in special porcelain tubes, the cerium used containing 95·6% Ce, with lanthanum and traces of iron, but free from neodymium and praseodymium. Nitrogen is used to protect against oxidation. Cerium of this degree of purity freezes at 775°. The freezing-point curve falls to a eutectic point at 635° and 5% of iron. On the rising branch of the curve a compound, $CeFe_2$, separates, which is changed at 773° to the compound Ce_2Fe_5. There is a second break in the curve at 1085°, where Ce_2Fe_5 breaks up into liquid and a solid solution rich in iron. This solid solution contains up to 15% of cerium at 1085°, diminishing on cooling to about 11% at 850° and lower temperatures. It undergoes two polymorphic changes due to those of iron, at 840°, determined thermally, and again at 795°, recognised by the appearance of magnetic properties on cooling. The change in saturation of the solid solution at these points, if any, is too small to be observed. Cerium, $CeFe_2$ and Ce_2Fe_5, do not form solid solutions.

The reactions in the solid state take place slowly, and there is difficulty in obtaining equilibrium. The compound $CeFe_2$ is magnetic at the ordinary temperature, but becomes non-magnetic at 116°. It is uncertain how far the second compound is magnetic, as the alloys contain the magnetic solid solution, which becomes non-magnetic at 795°. The hardness is a maximum at 60% of cerium.

The saturated solid solution is more resistant to oxidation than pure iron. The compounds are readily oxidisable, especially $CeFe_2$. The pyrophoric properties reach a maximum at 70% of cerium, and depend on the presence of one or other of the compounds. Pyrophoric cerium alloys usually consist of a hard compound embedded in a softer, readily oxidisable ground-mass. C. H. D.

Rare Earths. Edgar W. Engle and Clarence W. Balke (*J. Amer. Chem. Soc.*, 1917, **39**, 53—68).—A considerable quantity of a mixture of the rare earths has been fractionated first by the sodium sulphate method to remove the cerium earths from the yttrium earths and then by the bromate method to separate the yttrium earths. The bromate method is found to be efficient for concentrating erbium, yttrium, and dysprosium material. A comparative study was made of the permanganate and sulphuric acid volumetric methods for control of the fractionation. They have been found to give practically the same results in earth mixtures the bromates of which have a solubility near that of yttrium bromate. The dysprosium material obtained from the bromate fractionation was further purified by fractionation of the ethyl sulphates, and this material was very pure, and was used to determine the atomic weight of dysprosium. The method adopted consisted in the conversion of the oxide into chloride by the method used by Egan and Balke (A., 1913, ii, 508) for the atomic weight of yttrium. As a mean of six experiments, from the ratio $Dy_2O_3:2DyCl_3$ the value 164·228 was obtained for the atomic weight, which is considerably higher than the value accepted by the international Atomic Weight Committee. Dysprosium oxide is found to have $D_{4^\circ}^{27^\circ}=7{\cdot}81$. Dysprosium chloride is described as an olive-green mass, which dissolves slowly and completely in water with development of a considerable amount of heat. The solution is almost neutral to litmus, quite neutral to methyl-orange, faintly acid to phenolphthalein and to methyl-red. J. F. S.

The Structure of Metallic Coatings Prepared by the Metallic Spraying Method. Hans Arnold (*Zeitsch. anorg. Chem.*, 1917, **99**, 67—72).—Coatings prepared by Schoop's method of melting the end of a rod of metal and converting the molten drops immediately into spray by the action of a blast of air have been examined microscopically. Such coatings may be obtained in an adherent form even on paper or celluloid. The molten drops are elongated during their flight through the air, so that each has a long tail. The coatings have a fine waved or laminated structure, which is characteristic, and enables them to be distinguished from coatings obtained electrolytically or by other methods. The laminæ are due to the flattening out of the drops on reaching the surface. The union of the particles is a mechanical one, the fibres being felted together, and the evidence does not point to the formation of a true weld. Thus, successive spraying with zinc and copper leaves the two metals separate, and brass is not formed. C. H. D.

Cupric Cuprous Sodium Thiosulphate Ammoniate. Alfred Benrath (*Zeitsch. anorg. Chem.*, 1917, **99**, 5—10).—The salt described by Bhaduri (A., 1912, i, 597) as a cuprous sodium trithionate ammoniate is deep blue, which makes it improbable that it is a cuprous salt. It is identical with a salt previously prepared by several workers from sodium thiosulphate and ammoniacal copper solutions. The cupric content of the salt is determined by making a solution out of contact with air, and comparing the colour with that of a standard cupric solution. The ratio of $Cu^{\cdot}$ to $Cu^{\cdot\cdot}$ is found to be 2:1. The whole of the sulphur is present in the thiosulphate complex. The number of ammonia molecules is probably five. Regarding the cupric atom as the central atom, the formula becomes:

$$\left[(Cu_2S_2O_3)Cu(NH_3)_5\right]\begin{matrix}S_2O_3\\(Na_2S_2O_3)_2\end{matrix}.$$

It has not been found possible to prepare analogous compounds with potassium thiosulphate in place of sodium, or with ethylamine or pyridine in place of ammonia. Ethylenediamine gives a violet salt, having the composition $2CuS_2O_3,3C_2H_4(NH_2)_2,2H_2O$, in which the whole of the copper is in the cupric condition. C. H. D.

Non-aqueous Solutions. I. Reactions in *iso*Amyl Alcohol Solutions. Harry A. Curtis and Robert M. Burns (*J. Amer. Chem. Soc.*, 1917, **39**, 33—38).—The authors have carried out a number of reactions with inorganic substances in *iso*amyl alcoholic solution. Cobalt chloride is readily soluble in *iso*amyl alcohol, forming a deep blue solution; the cobalt is only partly precipitated by hydrogen sulphide, leaving a blue, supernatant solution. Ammonia precipitates the compound $CoCl_2,3NH_3$ as a pale rose-coloured powder. *Mercuric iodide* is only slightly soluble in cold *iso*amyl alcohol, but readily so in the hot liquid. On cooling a solution, the iodide separates in yellow crystals, which slowly pass into the red modification on keeping. Hydrogen sulphide causes the separation of an orange-red precipitate, which slowly becomes brown, and finally black if the stream of gas is continued, meanwhile, the solution takes on the odour of *iso*amyl mercaptan. If the solution is saturated with hydrogen chloride before the hydrogen sulphide is added, there is no precipitation of sulphide. *Mercuric chloride* behaves in much the same way as the iodide. *Copper chloride* forms a deep green solution, which on warming becomes brownish-green, the solution being almost opaque. Hydrogen sulphide precipitates the sulphide in a quantitative manner. Cadmium bromide added to the copper chloride turns the solution brown, owing to a double decomposition. Cadmium iodide solution precipitates cuprous iodide and liberates iodine; ammonia produces at first a green precipitate, which changes to a blue compound with more ammonia. The blue compound is unstable in the air and liberates ammonia, forming the green compound $CuCl_2,2NH_3$. Hydrogen chloride changes the colour of the solution to yellowish-brown. *Cobalt nitrate* is moderately soluble in *iso*amyl alcohol, forming a wine-red solution. The addition of hydrogen chloride changes the colour to blue; hydrogen sulphide quantitatively precipitates cobalt sulphide. Ammonia produces a dirty green precipitate. Cadmium bromide changes the colour to blue, owing to double decomposition. *Zinc chloride* is soluble in *iso*amyl alcohol to form a colourless solution. Ammonia precipitates $ZnCl_2,2NH_3$. *Cadmium iodide* solution in *iso*amyl alcohol is colourless. Hydrogen chloride liberates iodine, and ammonia precipitates $CdI_2,2NH_3$. Hydrogen sulphide precipitates a yellow compound which has the formula $CdI_2,2H_2S$. *Ferric chloride* dissolves in *iso*amyl alcohol to form an amber-coloured solution, which on keeping slowly deposits a rust-coloured precipitate. Hydrogen sulphide at first precipitates a dark brown compound, which changes to a straw-coloured compound with excess of hydrogen sulphide. *Selenium dioxide* is readily soluble in *iso*amyl alcohol, producing a solution which is acid to litmus. On keeping the solution for several days, the red modification of selenium separates out. Ammonia precipitates ammonium amyl selenite, $NH_4 \cdot SeO_3 \cdot C_5H_{11}$, a white compound, which on keeping in the air decomposes, red selenium separating. *Ammonium thiocyanate* is readily soluble in *iso*amyl alcohol. Hydrogen chloride precipitates ammonium chloride, and ferric chloride produces a blood-red coloration. *Methyl-orange* dissolves sparingly in *iso*amyl alcohol to form a yellow solution, which turns pink when shaken with an equal volume of *N*/2-hydrochloric acid, but when 0·125*N*-acid is used, only the aqueous layer becomes pink. The neutral tint can be obtained in the amyl alcohol solution by using 0·2*N*-hydrochloric acid. J. F. S.

Variation in the Physical Properties of Precipitated and Colloidal Manganese Dioxide from the Point of View of Physical Chemical Equilibrium. EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1917, **39**, 25—33).—In an earlier paper (A., 1915, ii, 461) it was stated that colloidal manganese dioxide prepared from aqueous solutions of dextrose and potassium permanganate in the presence of an alkali hydroxide undergoes colloidal transformations which vary with the conditions, and seem to be dependent on equilibria of an unknown nature. It has now been shown that the amorphous colloidal manganese dioxide obtained by reducing potassium permanganate with small quantities of acetone in the presence of variable amounts of potassium hydroxide (0—155 grams per litre) undergoes changes comparable with those of the emulsoid–suspensoid type of manganese dioxide. On the basis of certain results of other workers in this field, the author has made an attempt to interpret the experimental data for both types of colloids on the basis of two types of dynamic equilibria: (1) molecular association $\rightleftharpoons$ molecular dissociation, and (2) hydration $\rightleftharpoons$ dehydration. The experimental observations are found to agree readily with such an interpretation.

J. F. S.

A New Method for the Passification of Iron. A. SMITS and C. A. LOBRY DE BRUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 880—884).—On the assumption that there is an internal equilibrium between ferrous and ferric ions in metallic iron, and that the passive state is to be attributed to the disturbance of this equilibrium condition in the surface layers of the metal, it was anticipated that iron would become passive in contact with a solution of a ferric salt. Since it was probable that the nitrate ion would act as a negative catalyst in regard to the internal equilibrium, experiments were made with a solution of ferric nitrate. These experiments have given a positive result—in that the iron becomes passive if the temperature does not exceed a certain value, which depends on the concentration of the ferric nitrate solution. The greater the concentration, the higher is the limiting temperature.

It is shown that the passivity cannot possibly be attributed to the free nitric acid resulting from hydrolysis of the ferric nitrate, and the observations are considered to afford further support for the authors' views on the electromotive behaviour of metals.

H. M. D.

Dialysis. II. Hot Dialysis of the Chlorides of Ferric Iron, Chromium, and Aluminium, and the Rapid Preparation of their Hydrated Oxides. MARKS NEIDLE and JACOB BARAB (*J. Amer. Chem. Soc.*, 1917, **39**, 71—81. Compare A., 1916, ii, 475, 603).—A number of experiments have been carried out on the hot dialysis of ferric chloride and the chlorides of aluminium and chromium. The experiments were mostly carried out at 75—80° in parchment bags; two experiments were also made at the boiling point. The pure sols are obtained very rapidly. Hydrated aluminium oxide sol prepared at 75—80° is a slightly turbid and opalescent substance, from which, on keeping, a slight sediment settled. The hydrated chromic oxide sols were mobile, homogeneous, and clear green; in some cases they showed no tendency to gel after keeping for two months. The hydrated ferric oxide sols were of the yellow ochre variety; all had a tendency to settle, especially that prepared from the most concentrated ferric chloride. In very dilute solution, the whole of the ferric oxide sols were yellow, opalescent, and more stable. Pure hydrated chromic oxide sols are stable while hot, and gel slowly at the ordinary temperature. This leads to the conclusions that the higher the temperature the less electrolyte is necessary to stabilise the sol, and the attainment of adsorption equilibrium requires time at the ordinary temperature. It is also shown that the concentration of electrolyte necessary for stability at a given temperature increases with increase in the concentration of the colloid. The hydrated oxide sols have also been prepared by the addition of ammonium hydroxide to the chloride solutions and dialysing at 75—80°. The yield of colloid by this method in the case of iron is 89·9%, whilst in the case of aluminium and chromium it is only 53·3% and 41·3% respectively. This shows that in the last two cases the colloidal oxides are capable of passing through parchment paper. In the experiments conducted at the boiling point, a hydrated chromic oxide sol was obtained in ten hours which was purer than that obtained by dialysing a solution of chromic oxide in chromic chloride in the cold for seventy-three days. J. F. S.

The Hydrolysis of Cobalt and Nickel Acetate. K. A. VESTERBERG (*Zeitsch. anorg. Chem.*, 1917, **99**, 22—24).—The hydrolysis of these acetates has been determined by the extraction method (compare this vol., ii, 248). In 0·5*N*-solution at 18°, cobalt acetate is hydrolysed to the extent of 0·19% and nickel acetate to 0·43%. In 0·2*N*-solution at 18°, the hydrolysis of cobalt acetate is 0·16% and of nickel acetate 0·38%. The fact that the nickel salt appears to be more strongly hydrolysed in the 0·5*N*-solution is attributed to the salting out of acetic acid by the more concentrated solution.

Cobalt hydroxide is thus a stronger base than nickel hydroxide (compare Denham, T., 1908, **93**, 41). C. H. D.

Alkali Double Fluorides of Quadrivalent Elements. ANTON SKRABAL and JOSEF GRUBER (*Monatsh.*, 1917, **38**, 19—24).—The authors have prepared and examined a number of double fluorides of quadrivalent elements with the alkali metals. *Caesium stannifluoride*, Cs_2SnF_6, was prepared by adding a solution of cæsium carbonate in water to a solution of a stannic acid in 40% hydrofluoric acid and allowing to crystallise. It forms hexagonal crystals, which are optically negative uniaxial and consist only of the prism [10$\bar{1}$0] and the basal plane [0001]. *Rubidium stannifluoride*, Rb_2SnF_6, was prepared similarly to the cæsium salt; it separates at first as a gelatinous mass, which becomes crystalline if kept in contact with the mother liquor for several days. It forms hexagonal tablets which are optically negative uniaxial. *Caesium plumbifluoride*, Cs_2PbF_6, was prepared by dissolving lead acetate in cold hydrofluoric acid and adding cæsium carbonate. Crystals began to separate in several days; these were rhombohedral [$a:c=1:0·7855$]. *Rubidium plumbifluoride*, Rb_2PbF_6, was prepared similarly to the corresponding cæsium compound; these crystals were also rhombohedral [$a:c=1:0·7884$). *Caesium germanofluoride*, Cs_2GeF_6, was prepared by dissolving the dioxide of germanium in hydrofluoric acid and adding a solution of cæsium fluoride. A crystalline precipitate was formed on agitating the liquid. *Rubidium germanofluoride*, Rb_2GeF_6, was formed similarly to the corresponding cæsium compound. J. F. S.

The Zirconyl Radicle (ZrO). ED. CHAUVENET (*Compt. rend.*, 1917, **164**, 630—633).—From a study of the change in electrical conductivity of an *N*/100-solution of zirconium chloride during progressive treatment with an *N*/100-solution of sodium hydroxide, and also from measurements of the heat developed under similar conditions, the author concludes that the results obtained point to the existence of the radicle (ZrO) in zirconium compounds.
W. G.

Preparation of a Basic Bismuth Chlorate. L. VANINO and F. MUSSGNUG (*Ber.*, 1917, **50**, 323—324).—*Bismuth oxychlorate*, $BiOClO_3$, separates in long, glistening prisms on cooling a hot solution of bismuth nitrate (24·2) and sodium chlorate (96·8) in water (100). It does not react apparently when warmed with sulphur or charcoal and sulphur, but it detonates on heating with potassium cyanide. A mixture of bismuth nitrate (24) and sodium chlorate (64) gives a stable solution in 500—600 c.c. of water; such a solution is acid in reaction, but turns turmeric paper brown, this change being non-reversible, and it gives all the reactions of bismuth. Bismuth oxynitrate and chloride do not react in the same way; neither could a bromate or iodate be prepared.
J. C. W.

Preparation of Chloroplatinic Acid by Means of Hydrogen Peroxide. PAUL RUDNICK and R. D. COOKE (*J. Amer. Chem. Soc.*, 1917, **39**, 633—635).—It is shown that platinum-black dissolves entirely in a mixture of hydrochloric acid and hydrogen peroxide, forming chloroplatinic acid and thus preventing the formation of nitrosoplatinic chloride and chloroplatinous acid, two substances which very often are to be found in chloroplatinic acid prepared from aqua regia. These substances seriously affect the accuracy of potassium estimations by means of chloroplatinic acid. The method described for the preparation of chloroplatinic acid consists in covering 10 grams of platinum-black, dried, but not ignited, with 50 c.c. of concentrated hydrochloric acid. The mixture is heated to 50—60°, and hydrogen peroxide (3—30%) slowly added at such a rate that there is moderate evolution of chlorine. J. F. S.

Mineralogical Chemistry.

The Separation and Thermal Metamorphosis of the Zechstein Salts according to the Hypothesis of Rózsa. ERNST JÄNECKE (*Zeitsch. anorg. Chem.*, 1917, **99**, 1—4).—The view that the potash deposits consisted primarily of kainite and bischoffite has been opposed by Rózsa (this vol., ii, 97), who maintains that kieserite and carnallite represent the primary deposit. There is no available source from which the solutions rich in magnesium chloride, required by this hypothesis, could have come. The formation of primary kainite and bischoffite is a necessary consequence of the theory of double salts, and some of the equations given by Rózsa are theoretically impossible. C. H. D.

Halloysite from Colorado. ESPER S. LARSEN and EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1917, **7**, 178—180).—A white, dull, opaline clay occurs as the matrix of nodules of gearksutite in the fluor-spar mine at Wagon Wheel Gap, Colorado. It is optically isotropic with refractive index 1·47, increasing to 1·54 on exposure to air and to 1·55 after the material has been heated to 65°. Analysis agrees with the formula $Al_2O_3,2SiO_2,2H_2O,2aq$:

Al_2O_3.	CaO.	Na_2O.	SiO_2.	H_2O (below 100°).	H_2O (100—400°).	H_2O (>400°).	Total.*
35·58	0·77	0·10	40·09	8·60	2·12	12·88	100·14

* Also traces of Fe_2O_3, MgO, K_2O.

Occurring more abundantly in the same mine is another somewhat similar clay, which is also isotropic with *n* 1·557, but with the composition of kaolinite, $Al_2O_3,2SiO_2,2H_2O$. Halloysite is regarded as an amorphous mineral corresponding with kaolinite, but holding extra water, either by capillarity or adsorption, the formula being written as $Al_2O_3,2SiO_2,2H_2O,aq$. L. J. S.

Analytical Chemistry.

Some Main Lines of Advance in the Domain of Modern Analytical Chemistry. A. CHASTON CHAPMAN (T., 1917, **111**, 203—220).—A lecture delivered before the Chemical Society on March 15th, 1917. H. M. D.

A New Industrial Apparatus for the Estimation of Combustible Gases. ENRIQUE HAUSER (*Anal. Fis. Quim.*, 1917, **13**, 93—109).—A description of a new form of explosion pipette and absorption pipette for gas analysis. A. J. W.

Improved Nephelometer-Colorimeter. PHILIP ADOLPH KOBER (*J. Biol. Chem.*, 1917, **29**, 155—168).—The new instrument differs from the ordinary type of colorimeter, such as the Duboscq, in possessing movable cups instead of movable plungers. The heights of the cups are adjusted by means of a screw arrangement, with double milled head for rough and fine adjustment, which avoids the errors due to the lost motion inherent in racks and pinions. The plungers are made of black glass with fused-in, optically clear bottoms, and the bottoms of the cups are likewise fused in (not cemented), thus permitting the use of practically all solvents.

The author also describes a simple and convenient electric lamp with double adjustable reflectors which permit of the regulation of the amount of light reaching either side of the colorimetric field. The instrument can be furnished with an eye-support for keeping the eye steady, and also with attachable light filters for facilitating measurements with coloured fluids. Full directions for using and adjusting the instrument are appended. H. W. B.

Potassium Dichromate as a Standard. III. G. BRUHNS (*J. pr. Chem.*, 1917, [ii], **95**, 37—52. Compare A., 1916, ii, 337, 581).—Statements have been made that in the oxidation of potassium iodide solution by potassium dichromate in the presence of hydrochloric acid, the liberation of iodine sometimes occurs slowly, probably due to the intermediate formation of an iodochromate, $ICrO_3K$.

Such an observation, if real, might invalidate the use of potassium dichromate as a standard reagent, but after submitting the possibility of formation of iodochromate and of the gradual liberation of iodine to careful experimental examination, the author draws the conclusion that with dilute solutions no such danger is existent. D. F. T.

New Buffer Mixtures, Standard Tubes, and Colorimeter for Estimating the Hydrogen-Ion Concentration of Sea-water. J. F. McCLENDON (*Proc. Amer. Soc. Biol. Chem.*, 1916, xxx—xxxi; *J. Biol. Chem.*, 1917, **29**).—The two stock solutions used are: (1) 0·3*M*-boric acid containing 2·25% of sodium chloride, and (2) 0·075*M*-borax solution containing 1·9% of sodium chloride. They are mixed in thirty different proportions and sealed in 'Nonsol' tubes of 24 mm. bore. Thymolsulphophthalein and *o*-cresolsulphophthalein are employed as indicators, and the comparison with sea-water, which is contained in open tubes of the same bore, is carried out with a colorimeter having the lenses of a stereoscope placed in contact so as to bring the centres of the tubes together in a sharp line when viewed from the side with one eye 6 in. from the lenses. H. W. B.

The Interference of Thiocyanates, Ferrocyanides, and Ferricyanides in the Detection of Iodides with Palladium. Louis J. Curtman and Ben R. Harris (*J. Amer. Chem. Soc.*, 1917, **39**, 266—270. Compare this vol., ii, 108).—Thiocyanates, ferrocyanides, and ferricyanides all interfere with the detection of iodides by means of palladium chloride. An excess of palladium favours the detection of iodides in the presence of thiocyanates. The interference due to the presence of ferrocyanides and ferricyanides can, in most cases, be overcome by boiling the reaction mixture. W. G.

Estimation of Iodine in Mineral Water and in the Thyroid Gland. D. van Os (*Pharm. Weekblad*, 1917, **54**, 350—353).—Chloroform employed for the extraction of iodine should be free from alcohol. The difficulty is avoided by employing carbon disulphide or tetrachloride. A. J. W.

Iodometric Estimation of Sulphur Dioxide and the Sulphites. John B. Ferguson (*J. Amer. Chem. Soc.*, 1917, **39**, 364—373).—The author has made a critical experimental examination of the methods in general use for the estimation of sulphur dioxide in gas mixtures. For the very exact estimation of large or small amounts of sulphur dioxide, the excess iodine method is recommended. For small amounts only, either the excess iodine method or the Selby Smelter Commission method should be used, depending on which is the more convenient under the given working conditions. The Reich method may be used for either small or large amounts, but will yield accurate analyses only when sufficiently large samples are taken to render the uncertain end-point a negligible source of error. When carbon dioxide and sulphur dioxide are to be estimated in the same sample, the sulphite method can be used to advantage. With mixtures not above 3 or 4%, a suitable correction factor will render the results fairly accurate, but with higher concentrations the uncertainty increases. The author emphasises the following points to be observed in gas volumetric analysis: (1) The gas must nowhere come in contact with moisture prior to its reaching the absorbent. (2) The apparatus must be free from all rubber connexions when exact analysis of mixtures containing more than 10% of sulphur dioxide are to be made. For very accurate work, it is better to dispense with rubber entirely, although this source of error for mixtures containing less than 3% of sulphur dioxide may be neglected. (3) Mixtures of sulphur dioxide and air when dry do not interact appreciably, but when moist slow oxidation takes place. For this reason it is impossible to recover from a moist gas holder, even by pumping, the initial amount of sulphur dioxide if the gas has been kept for any great length of time. The author recommends the following procedure for the analysis of such soluble sulphites as sodium sulphite. The solid salt is dissolved directly in an excess of an iodine solution containing sufficient hydrochloric acid, and the excess iodine is estimated with thiosulphate. This eliminates several sources of error due to oxidation of the salt by agents other than the iodine solution. J. F. S.

Detection and Estimation of Small Quantities of Free Sulphuric Acid in the Presence of Sulphates. E. Vulquin and M. Entat (*Ann. Chim. anal.*, 1917, **22**, 61—66).—Measurements are made of the conductivity of the solution while it is titrated with barium hydroxide solution; the burette readings are plotted against the conductivity figures, and the curve exhibits an inflexion at the point where the free sulphuric acid has been neutralised. The differences in potential are measured between a rotating polarised platinum electrode and a normal calomel electrode, both placed in the solution (compare Dutoit and von Weisse, A., 1911, ii, 1129). The method is suitable for estimating quantities of 0·005 gram of sulphuric acid in the presence of sulphates, organic acids, and mineral and organic salts. W. P. S.

New Reagent for the Separation of Ammonia. I. Colorimetric Estimation of Ammonia in Urine. Otto Folin and Richard D. Bell (*J. Biol. Chem.*, 1917, **29**, 329—335. Compare Folin and Denis, A., 1916, ii, 574).—The authors recommend "permutit" as a substitute for Merck's purified blood charcoal in the method for the estimation of ammonia previously published. Permutit absorbs the ammonia from neutral or slightly acid solutions, and the permutit–ammonia compound is decomposed on Nesslerisation with the production of the normal colour. The permutit may be collected, washed, and used again repeatedly.
H. W. B.

Micro-titration of Ammonia. George D. Barnett (*J. Biol. Chem.*, 1917, **29**, 459—462).—See this vol., i, 359.

"Nitron" as a Gravimetric Reagent for the Analysis of Substances used in Explosives. W. C. Cope and J. Barab (*J. Amer. Chem. Soc.*, 1917, **39**, 504—514).—For the most part a summary of previous work on the use of "nitron" as a precipitant in the estimation of nitric acid, perchloric acid, picric acid, and their salts, a full bibliography being given. The use of "nitron" has been extended to the estimation of trinitrocresol and its salts under conditions similar to those for picric acid (compare Busch and Blume, A., 1908, ii, 328). In the presence of sulphuric acid, dinitrophenol does not give a precipitate with "nitron," this forming the basis for a simple method for the estimation of mixtures of di- and tri-nitrophenols. Busch's method for estimating "nitrocellulose" (compare A., 1906, ii, 708) can be used for "nitromannitol" and "nitrostarch," but for "nitroglycerin" it is necessary to use 30% hydrogen peroxide. W. G.

The Volumetric or Pemberton Method for Estimating Phosphoric Acid, with some Experiments showing the Influence of Temperature and the Sulphuric Acid Radicle on the Results. PHILIP McG. SHUEY (*J. Ind. Eng. Chem.*, 1917, **9**, 367—370).—Very varying results are obtained, according as the precipitation is carried out at various temperatures over the range 5—65°. The most satisfactory conditions are to precipitate at 30°, the molybdic acid solution added being also at that temperature. It is advisable when precipitating from a sulphuric acid solution to add at least 5 grams of ammonium nitrate. Old molybdate solutions from which molybdic acid tends to separate should not be used, as they seriously affect the results. W. G.

Detection of Carbon in Inorganic and Organic Substances. ERNST MÜLLER (*J. pr. Chem.*, 1917, [ii], **95**, 53—54).—A mixture of approximately 0·02 gram of the substance under investigation with roughly twenty times its weight of potassium azide is cautiously heated, at first gently and then, finally, for two minutes at a red heat. Potassium cyanide is formed, and may be recognised in the usual way by conversion into Prussian blue.

The test, which may be rendered still more delicate by the additional presence of a little metallic potassium in the reaction mixture, can not only be applied to organic compounds, but also to steel and carborundum. D. F. T.

The Penfield Test for Carbon. W. G. MIXTER and F. L. HAIGH (*J. Amer. Chem. Soc.*, 1917, **39**, 374—375).—The authors describe a test, due to S. L. Penfield, for the detection of carbon in minerals and metals. The method consists in heating an intimate mixture of lead chromate and the substance in a narrow, horizontal, hard glass tube which has a small bulb blown in the underside of it near the open end. In the experiment, this bulb contains a drop of a saturated solution of barium hydroxide. The formation of a white film of barium carbonate on the liquid indicates the presence of carbon in the substance. The lead chromate is prepared by precipitation, and any accidental admixture of carbon from dust is removed by heating it in oxygen in the tube before the experiment. A series of experiments is described. A mixture of 9·990 grams of alumina and 0·010 gram of silicon carbide was made, and various quantities of this were mixed with the lead chromate and the test carried out. It is shown that 10 mg.

cooled quickly. The acid solution is neutralised with 0·1*N*-sodium hydroxide, using phenolphthalein as indicator, and adding from time to time sodium phosphate solution. When titration is complete, the volume of phosphate solution added should be one-half the volume of the iodine solution. The arsenious oxide solution is then titrated with 0·1*N*-iodine solution. J. F. S.

Titration of some Bivalent Metal Sulphates by the Conductance Method. Herbert S. Harned (*J. Amer. Chem. Soc.*, 1917, **39**, 252—266).—It is shown that the change in the electrical conductivity of solutions containing sulphates of certain metals, on the addition of a solution of barium hydroxide, affords a method for the estimation of the metals in question. The apparatus employed permits of the measurements being carried out in an atmosphere containing carbon dioxide.

The method is applicable to the estimation of magnesium, copper, nickel, and cobalt in solutions containing the respective sulphates. It may also be used in the estimation of magnesium in a solution containing magnesium sulphate, calcium sulphate, and sulphuric acid, and hence is suitable for the estimation of magnesium in a dolomite. Results obtained with cadmium sulphate indicate the formation of a basic sulphate of the composition $CdSO_4,3Cd(OH)_2$. H. M. D.

Method for the Separation of Lead and Iron. J. F. Sacher (*Chem. Zeit.*, 1917, **41**, 245).—The process depends on the insolubility of basic ferric nitrate; it is useful for the separation of very small amounts of iron from lead salts. Two grams of the lead salt containing iron are heated on a water-bath with an excess of nitric acid (D 1·15), the mixture is then evaporated, and the residue heated at 100° for about fifteen minutes. The residue is now treated with hot water, the insoluble portion collected on a filter, washed, then dissolved in hot dilute hydrochloric acid; the iron is precipitated from this solution as hydroxide by the addition of ammonia, and the precipitate is collected, washed, ignited, and weighed. If the substance under examination contains silicates which are decomposed by nitric acid, the residue obtained after the evaporation of the nitric acid must be heated at 125°; lead nitrate does not undergo the slightest decomposition at this temperature. Should lead sulphate be present, the residue is extracted with ammonium acetate solution before the basic iron salt is dissolved in hydrochloric acid. W. P. S.

Detection of Traces of Mercury Salts for Toxicological Purposes. Kendall Colin Browning (T., 1917, **111**, 236—240).—The method described, a development of the Dupré method of detecting mercury in explosives, involves the electrolytic deposition of the mercury on a gold cathode, which is then washed with water and introduced into a Dupré tube heated at 200—250°, the mercury being detected by its spectrum. The best conditions for electrolysing the mercury solution and for making the spectroscopic observations have been determined as the result of systematic tests.

It was found that the mercury spectrum is shown when 200 c.c. of a solution containing one part of mercuric chloride in a thousand million is electrolysed for ten minutes, using a current of two amperes.

Very dilute solutions of mercuric salts show a loss of mercury when kept in soft glass or even in ignited quartz glass bottles. If such solutions are evaporated with the object of concentrating the mercury salts, there is also a very appreciable loss.

H. M. D.

Estimation of Mercury in Basic Mercuric Salicylate and its Isomerides. H. Lajoux (*J. Pharm. Chim.*, 1917, [vii], **15**, 241—246).—Rupp has shown (A., 1901, ii, 348) that the mercury in mercury salicylate in hydrochloric acid solution is not converted into mercury sulphide by treatment with hydrogen sulphide, and that only when the mixture is heated at 100° does the formation of sulphide take place; even then the action is very slow and attended with risk of incomplete decomposition of the intermediate compound which is first formed. The following method, in which the salicylate is decomposed with potassium cyanide, is therefore recommended. A weighed quantity of 0·25 gram of the mercury salicylate or of its isomerides is mixed with 1·25 grams of potassium cyanide and 25 c.c. of water, the solution is heated, and saturated with hydrogen chloride, care being taken not to inhale the vapours given off at this stage of the process. The solution is now diluted with boiling water to about 150 c.c., and, while hot, treated with a current of hydrogen sulphide. The mercury is precipitated completely as sulphide within a few minutes, and the precipitate is collected, washed, and weighed. The mercury may also be estimated volumetrically after the salicylate has been decomposed by sulphuric acid or aqua regia. One gram of the substance is heated on a water-bath for a few minutes with 10 c.c. of concentrated sulphuric acid, and the violet solution is diluted to 100 c.c.; or the same quantity of the substance is boiled with 4 c.c. of hydrochloric acid and 2 c.c. of nitric acid, potassium chlorate is added, and the colourless mixture then diluted to 100 c.c. Twenty c.c. of the solution (obtained by either of these treatments) are then added to a flask containing 10 c.c. of ammonia, 10 c.c. of $N/10$-potassium cyanide solution, 1 c.c. of 10% potassium iodide solution, and 60 c.c. of water, and the mixture is titrated with $N/10$-silver nitrate solution until a persistent opalescence is obtained. The quantity of mercury present is calculated from the volume of silver nitrate solution used. Approximately one-half of the quantity of mercury is found if the salicylate is dissolved directly in potassium cyanide solution, then treated with ammonia, potassium iodide, and water, and the solution titrated with silver nitrate solution. Basic mercuric salicylate should contain 59·52% of mercury, but commercial samples rarely contain more than 57%. W. P. S.

Differential Iodometry. III. Estimation of the available Oxygen in Soluble and Precipitated Oxidised Forms of Manganese. O. L. Barnebey and W. C. Hawes (*J. Amer. Chem. Soc.*, 1917, **39**, 607—610. Compare following abstract).—Methods are described for the estimation of the available oxygen in commercial permanganates, precipitated highly oxidised manganese oxides, and some forms of pyrolusite, all of which contain some iron. In the case of potassium permanganate containing ferric sulphate, 10 c.c. of *N*-potassium iodide and 10 c.c. of 2*N*-phosphoric acid are added, the mixture is allowed to react for three minutes, and the iodine titrated with thiosulphate. The results are extremely good. With precipitated oxides of manganese, and such samples of natural pyrolusite as do not contain much iron, the weighed sample is treated with 10 c.c. of *N*-potassium iodide and 10 c.c. of 2*N*-phosphoric acid, and kept at the ordinary temperature for fifteen minutes. Then the liberated iodine is titrated with sodium thiosulphate. The estimations were controlled by the Bunsen distillation method, and an extremely good agreement between the two values obtained. In cases of pyrolusite which contains much iron, the reaction takes place very slowly and does not easily go to completion, hence the method is not to be recommended in such cases. J. F. S.

Differential Iodometry. II. The Titration of Chromic Acid in the Presence of Ferric Iron and the Analysis of Chromite for its Chromium Content. O. L. Barnebey (*J. Amer. Chem. Soc.*, 1917, **39**, 604—606. Compare A., 1915, ii, 574; 1916, ii, 261).—A method has been worked out for the iodometric estimation of chromic acid in the presence of ferric iron. An aqueous solution of the sample is made just alkaline with sodium hydroxide, then solid sodium peroxide is added in slight excess. The solution is boiled for a few minutes to decompose the excess of peroxide, and it is then made acid with phosphoric acid, a sufficient excess of which is added to dissolve completely the ferric phosphate and make the solution about 3*N*-phosphoric acid. Ten c.c. of *N*-potassium iodide are added for every 100 c.c. of solution, and the liberated iodine is titrated with sodium thiosulphate. In this reaction the whole of the liberated iodine is due to the chromic acid, since the ferric phosphate is only slightly ionised and its velocity of reaction with potassium iodide is very small. The analysis of chromite is conducted as follows. A sodium peroxide fusion is made; this is extracted with water and the solution boiled. The solution is acidified with sufficient excess of phosphoric acid to make a 3*N*-solution, potassium iodide is added, and the liberated iodine titrated with thiosulphate. The results of several analyses are given, in which the chromium has been estimated both gravimetrically and volumetrically; the agreement between the two estimations is extremely good. J. F. S.

The Estimation of Molybdenum by Potassium Iodate. GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1917, **39**, 246—249).—It is shown that molybdenum in the form of molybdate may be accurately estimated by the use of iodic acid. The molybdate solution, acidified with hydrochloric acid, is heated to 50° and allowed to pass slowly through a column of amalgamated zinc into a 500 c.c. flask containing 5 c.c. of iodine monochloride solution, 25 c.c. of concentrated hydrochloric acid, 5 c.c. of water, and 7 c.c. of chloroform, the flask being cooled by immersion in a bath of cold water. The liquid is then titrated with potassium iodate, the reaction taking place corresponding with the equation $KIO_3 + Mo_2O_3 + 2HCl = KCl + Mo_2O_5 + ICl + H_2O$. The end-point is quite sharp, although the rapid reaction in question is followed by a relatively slow reaction, in which the molybdenum is oxidised to MoO_3. To prevent hydrolysis of the iodine monochloride it is important that the solution in the flask should contain not less than 10% of hydrochloric acid. H. M. D.

Alleged Ninhydrin Reaction with Glycerol, etc. VICTOR JOHN HARDING (*Proc. Amer. Soc. Biol. Chem.*, 1916, xiv; *J. Biol. Chem.*, 1917, **29**).—The author finds that specimens of glycerol of different origin behave differently towards ninhydrin, and concludes that a positive ninhydrin reaction with glycerol is really due to the presence of nitrogenous impurities. H. W. B.

Estimation of Cholesterol in Blood. W. R. BLOOR (*J. Biol. Chem.*, 1917, **29**, 437—445. Compare Weston, this vol., ii, 156).—The author discusses possible reasons for the inconsistency of the results obtained by Weston for the cholesterol in blood estimated by Bloor's method. H. W. B.

Cholesterol. III. Influence of Bile Derivatives in Bloor's Method of Estimation of Cholesterol. GEORGINE LUDEN (*J. Biol. Chem.*, 1917, **29**, 463—476).—A modified Liebermann reaction for cholesterol is given by cholesterol-free gall-stones. The difference in the results afforded by Bloor's original and his modified methods for the estimation of cholesterol (A., 1916, i, 176; ii, 275) is probably due to the participation in the latter method of biliary pigments and acids in the reaction. The figures given by the modified method are always higher, and the difference between the results obtained by the two methods may possibly furnish useful information in cases of biliary disturbance with or without jaundice. H. W. B.

Separation of Cholesterol and Phytosterol from Fats and Oils by means of Digitonin. J. PRESCHER (*Zeitsch. Nahr. Genussm.*, 1917, **33**, 77—80. Compare A., 1916, ii, 499).—The digitonin reagent used should contain 1% of the substance in 96% (by vol.) of alcohol; two kinds of digitonin are sold, one being a crystalline substance which is insoluble in water, whilst the other is amorphous and soluble in water. The former is the better precipitant for cholesterol and phytosterol. In place of chloroform, ether, etc., other solvents, such as dichloroethylene, perchloroethylene, or pentachloroethane, might be employed to remove the fat from the digitonin precipitate, but their suitability for the purpose requires proof. W. P. S.

A New Reaction Distinguishing the Sugars. Luis Guglialmeli (*Ann. Soc. Quim. Argentina*, 1916, **4**, 277—282).—An application of Sánchez's fluorescent reaction to distinguish sugars (*ibid.*, 1915, **3**, 305). A. J. W.

Improved Method of Estimating Sugar in the Urine and Blood. P. J. Cammidge (*Lancet*, 1917, i, 613—614).—The author finds the iodometric estimation of sugar by Scales's method (A., 1916, ii, 117) to be both accurate and rapid, and applies it to a modified Benedict solution, which is ten times as sensitive to reducing sugars as Fehling's solution, and keeps indefinitely. Details for the estimation of sugar in urine and blood are given; of the latter, 0·1—0·2 c.c. suffices. G. B.

Thiobarbituric Acid as a Qualitative Reagent for Ketohexose. G. P. Plaisance (*J. Biol. Chem.*, 1917, **29**, 207—208).—The substance to be tested is placed in a test-tube and sufficient hydrochloric acid and water are added to bring the acid concentration to 12%. The tube is heated over a free flame until boiling begins. It is then cooled and a few drops of a thiobarbituric acid solution in 12% hydrochloric acid are added. If a ketohexose was originally present, an orange-coloured precipitate forms on keeping. If only aldoses are present, the solution may become yellow, but a precipitate is not formed. Barbituric acid cannot be used instead of thiobarbituric acid, because the condensation product is much more soluble. When larger concentrations of hydrochloric acid are employed, slight precipitates may also be obtained from aldoses. H. W. B.

The Determination of the Gelatinisation Temperatures of Starches by means of an Electrically Heated Chamber on the Microscope Stage. Arthur W. Dox and G. W. Roark, jun. (*J. Amer. Chem. Soc.*, 1917, **39**, 742—745).—A slight modification of the method of Francis and Smith (compare *J. Ind. Eng. Chem.*, 1916, **8**, 509), the hot water circulating device being replaced by an electric incubator for the microscope stage. The necessary temperature correction was ascertained by determining in the apparatus the melting points of three organic substances, the melting points of which cover the range of gelatinisation temperatures. The gelatinisation temperatures of the starches from a large number of different varieties of maize were determined, and, whilst no difficulty was found in getting concordant results for a given variety, the results varied between 64·1° and 71·1° for the different sorts. W. G.

Nitrogen in Amino-form as Estimated by Formaldehyde-titration, in Relation to some other Factors Measuring Quality in Wheat Flour. C. O. Swanson and E. L. Tague (*J. Amer. Chem. Soc.*, 1917, **39**, 482—491).—Estimations of ash, acidity, total nitrogen, and nitrogen in amino-form as given by the formaldehyde titration (compare Sorensen, *J. Amer. Chem. Soc.*, 1916, **38**, 1098) have been made on a number of samples of flour collected from different mills and also on one set of mill-stream flours from a medium-sized mill. The results show that nitrogen in amino-form, as measured by the formaldehyde-titration, is valuable, together with the ash and acidity, in measuring quality in flour. It should be noted, however, that titratable nitrogen is more uniformly distributed in the wheat kernel than are the materials which determine the amount of ash and acidity. The increase in titratable nitrogen is, therefore, not proportionate to the increase in ash or acidity in clear and low-grade flours, as compared wth patent and straight flours made from the same sound wheat. W. G.

The Duclaux Method for the Estimation of the Volatile Fatty Acids. FRED. W. UPSON, H. M. PLUM, and J. E. SCHOTT (*J. Amer. Chem. Soc.*, 1917, **39**, 731—742).—The authors have redetermined the Duclaux constants (compare A., 1896, ii, 504) for formic, acetic, and propionic acids and do not find close agreement. Working with mixtures of these acids, it is found that small, unavoidable experimental errors may vitiate the results, that when more than two acids are present in a mixture almost identical series of results may be calculated from mixtures of the acids in quite different proportions, and further, that results which, from the constants, indicate the presence of only one acid, may just as well be calculated in terms of three or more acids. Small amounts of acids in a mixture may just as well be distributed between the acids next higher and lower in the series. W. G.

The Duclaux Method for Volatile Fatty Acids. A. R. LAMB (*J. Amer. Chem. Soc.*, 1917, **39**, 746—747).—Contrary to the conclusions of Upson, Plum, and Schott (preceding abstract), the author considers that accurate results can be obtained with Duclaux's method, working under carefully defined conditions and using electrical heating for the distillation, provided that no attempt is made to determine more than two or three acids in the same fraction. The main essential is to use highly purified acids for the preliminary determination of the constants.

W. G.

Studies in Steam Distillation. Some Applications of Duclaux's Method. H. DROOP RICHMOND (*Analyst*, 1917, **42**, 133—138).—Duclaux's method is trustworthy for the estimation of butyric acid in acetic anhydride, and it is shown that a combination of the usual titration methods and the Duclaux method will give the quantities of acetic anhydride, acetic acid, and butyric acid present in a sample. An examination of the acid obtained by hydrolysis of the acetanilide formed would indicate what proportion of the butyric acid was present as anhydride. Acetyl chloride may be examined in the same way; samples of this substance examined by the author did not contain butyric acid. Duclaux's method is also suitable for testing the purity of substituted malonic acids. W. P. S.

Separation and Estimation of Butyric Acid in Biological Products. I. I. K. Phelps and H. E. Palmer (*J. Biol. Chem.*, 1917, **29**, 199—205).—The authors find that butyric acid can be separated from mixtures containing formic, acetic, and butyric acids by means of the solubility of quinine butyrate and the insolubility of quinine acetate and quinine formate in carbon tetrachloride. The actual amount of butyric acid may be estimated by weighing the quinine butyrate, which may be crystallised and identified by its melting point (77·5°). The solubilities of the quinine salts of propionic and butyric acids in carbon tetrachloride are too similar to allow of a separation being effected by fractional crystallisation. H. W. B.

The Identification and Estimation of Lactic Acid in Biological Products. I. K. Phelps and H. E. Palmer (*J. Amer. Chem. Soc.*, 1917, **39**, 136—149).—The lactic acid is esterified by means of alcohol vapour containing dry hydrogen chloride passed through the mixture containing the lactic acid, suspended in vaselin at 100—110°, using zinc chloride as a second catalyst. The ethyl lactate passes over along with any other esters of low boiling point, whilst esters such as the citrate and tartrate remain in the flask. The distillate is fractionally distilled through a Hempel column, any ethyl formate and acetate, together with a large proportion of the propionate and butyrate present, being thus removed. The residue in the flask which contains the ethyl lactate is hydrolysed with barium hydroxide, and the acids converted into their quinine salts. Quinine lactate is separated from the butyrate and propionate by reason of the much greater solubility of the latter salts in carbon tetrachloride. The quinine lactate is weighed and identified by its melting point. It is essential, in this estimation, that the aqueous solutions of quinine lactate should not be allowed to remain, and especially that they should not be heated, but should be evaporated by distillation under diminished pressure. If this precaution is not observed, quinotoxine lactate may be formed, and this is much more soluble in carbon tetrachloride than quinine lactate.

In the absence of propionic and butyric acids, lactic acid may also be estimated as guanidine lactate. W. G.

Influence of Calcium Tartrate on the Estimation of Total Tartaric Acid (in Crude Tartars). P. Carles (*Ann. Chim. anal.*, 1917, **22**, 71—72).—The Goldenberg method sometimes gives low results when applied to crude tartars containing a large proportion of calcium tartrate; this is probably due to incomplete decomposition of the calcium tartrate during the treatment with potassium carbonate. It is recommended that the hydrochloric acid solution of the sample should be added gradually, with constant stirring, to the potassium carbonate solution, and the mixture then boiled until all hydrogen carbonates have been decomposed; the mixture should now be alkaline to phenolphthalein. The presence of undecomposed calcium tartrate is indicated if the separated and washed calcium carbonate is not completely soluble in acetic acid. W. P. S.

A Method for the Examination of Methyl Salicylate. Alan R. Albright (*J. Amer. Chem. Soc.*, 1917, **39**, 820—825).—In examining a sample of methyl salicylate, it is first benzoylated, thus converting the true methyl salicylate and any other phenolic substances present into crystalline benzoates. The crystalline product is mounted on an object slide, using a liquid equal in refractive index to the mean index of methyl *o*-benzoyloxybenzoate. Then, when examined with a petrographic microscope, the salicylate derivative becomes invisible, leaving other compounds in clear view, thus facilitating their identification by means of their optical properties. Using this method, phenol has been found both in synthetic and pure, natural methyl salicylate. In some synthetic methyl salicylates, the methyl ester of *p*-hydroxytoluic acid has been detected in very small amount, but not in the natural oil. A substance closely resembling methyl *p*-hydroxybenzoate also occurs in the synthetic ester, but not in genuine oils of wintergreen or birch. W. G.

Quick Titration Method for Estimating Small Amounts of Uric Acid. J. Lucien Morris (*Proc. Amer. Soc. Biol. Chem.*, 1916, xiii; *J. Biol. Chem.*, 1917, **29**).—The uric acid is separated from the urine, blood, or other fluid by precipitation as zinc urate, and is then titrated in acetic acid solution with *N*/200-potassium permanganate solution. H. W. B.

Value of the Determination of the Freezing-point in the Examination of Milk. J. J. Polak (*Chem. Weekblad*, 1917, **14**, 323—324).—The author considers that the freezing-point method affords the most trustworthy test for the presence of water in milk. A. J. W.

Titration Method for Estimating Minute Quantities of Acetone. Roger S. Hubbard (*Proc. Amer. Soc. Biol. Chem.*, 1916, xiv; *J. Biol. Chem.*, 1917, **29**).—The modification of the Messinger method described by the author consists chiefly in the employment of standard solutions of iodine and thiosulphate of *N*/100- or *N*/500-strengths. H. W. B.

[Estimation of Creatinine and Total Creatinine (Creatinine and Creatine) in Whole Blood]. D. Wright Wilson and E. D. Plass (*J. Biol. Chem.*, 1917, **29**, 413—423).—See this vol., i, 360.

The Qualitative Identification of the Drugs containing Emodin. George D. Beal and Ruth Okey (*J. Amer. Chem. Soc.*, 1917, **39**, 716—725).—The authors have devised a tentative scheme for the identification of the drugs cascara, rumex, rhubarb, frangula, senna, and aloes.

A small amount of a dilute alcoholic solution of the drug preparation is shaken with four times its volume of benzene. A small portion of the benzene extract is shaken with 30% aqueous sodium hydroxide, when a permanent coloration varying from light red to deep violet is obtained if one of the drugs is present. If the test is positive, another portion of the benzene extract is evaporated to dryness, moistened with concentrated nitric acid, and evaporated again. The residue will be red or orange-red, and when moistened with a solution of potassium cyanide in potassium hydroxide will become red or purplish-red if one of the drugs is present.

For the identification of the individual drug, one portion of the alcoholic solution is shaken with four volumes of benzene, the benzene extract drawn off, and the extraction repeated with amyl alcohol. Another portion of the dilute alcoholic solution is extracted with ethyl ether. A portion of the benzene extract is shaken with concentrated aqueous ammonia, a deep reddish-violet colour and precipitate indicating the presence of rhubarb, which may be confirmed by shaking another portion of the benzene extract with lead subacetate, a yellowish-orange precipitate turning red with alkali confirming the presence of rhubarb.

A portion of the amyl alcohol extract is shaken with strong aqueous ammonia. A deep red colour with a dark green fluorescence indicates aloes or a freshly prepared extract of cascara. If the test is positive, another portion is shaken with mercurous nitrate; a red colour in the aqueous layer indicates aloes, which may be confirmed by the cupraloin test (compare Klunge, *Chem. Zeit.*, 1880, **4**, 1085), the hydrogen peroxide test (compare Hirschsohn, *Pharm. Zentr.*, 1901, **42**, 63), or the fluorescence test with borax. The presence or absence of cascara may be proved by evaporating a portion of the benzene or amyl alcohol extract, nitrating, and treating with stannous chloride. Cascara will give a deep red colour, aloes a yellowish-brown.

A portion of the ether extract is shaken with an equal volume of saturated nickel acetate solution, when a red, aqueous layer indicates senna. If the solution retains its green colour and gives a green precipitate with potassium hydroxide, rumex is present. If on shaking this mixture with potassium hydroxide a violet precipitate is formed, senna is indicated, whilst with rhubarb or frangula it will be reddish-violet, and with cascara dark orange-red.

If the above tests are not conclusive, a portion of the ether extract is evaporated, nitrated, and reduced with stannous chloride at 100°. Senna gives a green residue, aloes a brown one, cascara red, rumex, rhubarb, and frangula violet-red, frangula being the deepest. The residues are washed with water to remove the stannous chloride, and a drop of sodium hypochlorite solution added. Senna alone develops a distinct red colour, the others turning yellow before decolorisation. W. G.

General and Physical Chemistry.

Absolute System of Colours. II. WILHELM OSTWALD (*Zeitsch. physikal. Chem.*, 1917, **92**, 222—226. Compare A., 1916, ii, 205).—The general equation expressing colour in the author's system involves three terms connected by the relation $r+w+s=1$, where r refers to a pure colour, w represents white, and s black. The determination of the pure colour factor r in terms of the frequency of light in the visible spectrum is discussed, and a table is given showing the relation between the frequency and the classification of the various colours according to the author's system.

H. M. D.

Determination of the Spectrum of a Univalent Polyatomic Ion, and in Particular of the $H^{\bullet}_2$ Ion. J. STARK (*Ann. Physik*, 1917, [iv], **52**, 221—254).—In a further attempt to differentiate the carriers which are responsible for the spectra which are emitted under different conditions, it has been found that the many-lined spectrum of hydrogen is to be attributed to diatomic hydrogen ions carrying a single positive charge. The spectrum in question is excited in greater intensity by low-speed cathode rays (20—50 volts), whereas the canal rays give rise to a very feeble emission of the many-lined spectrum. It is not yet known whether the visible spectrum attributable to the $H_2^{\bullet}$ ions is accompanied by a characteristic emission in the ultra-red or in the ultra-violet.

The above-mentioned spectrum of the univalent diatomic hydrogen ion is discussed in reference to the spectra emitted by the univalent, monatomic hydrogen ion, the hydrogen atom, and the hydrogen molecule.

H. M. D.

The Emission of a Continuous Spectrum in the Combination of an Electron with a Positive Ion. J. STARK (*Ann. Physik*, 1917, [iv], **52**, 255—275).—The fact that hydrogen gives rise to a continuous spectral emission in the near ultra-violet has been noted by several observers, but the conditions under which this is obtained have not previously been submitted to investigation. New experiments show that there are two continuous hydrogen spectra, one of which is situated in the ultra-violet at about λ 2500 and the other in the bluish-violet region. The emission phenomena in question are associated with the presence of positively charged ions in the gas, the bluish-violet spectrum being connected with the $H_2^{\bullet}$ ion and the ultra-violet with the $H^{\bullet}$ ion. The intensity of the two spectra is greatest under conditions in which combination between electrons and positive ions is of greatest frequency. The bluish-violet emission is accordingly of high intensity in the blue layer at the commencement of the positive column, whilst the ultra-violet continuous spectrum is emitted in high intensity by the hydrogen canal rays.

Continuous spectra are also emitted by the vapours of the alkali and alkaline earth metals, cadmium, and mercury, and in these cases also the emission is dependent on the presence of positively charged metal ions. The frequency with which these ions combine with electrons determines the intensity of the continuous spectra, and these are accordingly emitted by the positive column in glow discharge through the vapour, and in the case of the alkali and alkaline earth metals by the Bunsen and oxyhydrogen flames in which the vapours are present.

It is suggested that all the elements will probably give rise to a continuous emission spectrum of the above-mentioned type under favourable conditions. According to the nature of the element, this spectrum may be situated in the visible, ultra-red, or ultra-violet region. H. M. D.

Spectroscopic Observations on the Active Modification of Nitrogen. V. Hon. R. J. Strutt (*Proc. Roy. Soc.*, 1917, [*A*], **93**, 254—267).—The faint red bands λ 6394·45, λ 6468·53, λ 6544·81, and λ 6623·52 observed in the spectrum of the nitrogen afterglow have been further examined under conditions which preclude the possibility that they are to be attributed to the light of stray discharges in the observation tube. These bands, which belong to the α-group, are found in undiminished intensity when stray electric discharges are rigidly excluded, and are therefore characteristic of the afterglow spectrum.

The β- and γ-groups of bands appear in most cases with the same relative intensities, and it has been previously suggested that they are both due to oxides of nitrogen. The brightness of the visual afterglow (α-group) is enhanced in presence of small quantities of other substances which act as catalysts, and it is found that those substances which yield oxygen increase the intensity of the β-group, whilst catalysts which do not yield oxygen brighten up the visual afterglow, but have no influence on the intensity of the β- and γ-groups of bands. By subjecting the nitrogen used to the action of a concentrated alkaline solution of pyrogallol and of phosphoric oxide in order to remove oxygen, carbon dioxide, and water as far as possible, it has been found that the intensity of the β- and γ-groups of bands is greatly reduced. From experiments with nitrogen purified in this manner, it appears that the addition of oxygen or nitric oxide to the afterglow brings out the β- and γ-bands with a certain relative intensity. The addition of carbon dioxide gives greater relative intensity to the β-bands and carbon monoxide to the γ-bands. The addition of sufficient quantities of nitric oxide or nitrogen peroxide to the afterglow causes the β- and γ-groups to disappear, and a visually greenish, continuous spectrum is then obtained. The same spectrum, together with the γ-, but not the β-group, appears when nitric oxide is passed into a blow-pipe flame.

The introduction of oxygen into the afterglow is not accompanied by any measurable oxidation, and for this reason it does not seem possible to attribute the β- and γ-groups of bands to nitric oxide. H. M. D.

The *L*-Series of the Elements of High Atomic Weights. R. LEDOUX-LEBARD and A. DAUVILLIER (*Compt. rend.*, 1917, **164**, 687—690. Compare Moseley, A., 1914, ii, 14; and Barnes, A., 1915, ii, 658).—A study of the *L*-series of radiations in the cases of tungsten, iridium, platinum, and gold. The series comprises nine rays, which occur independently of the mode of generation of the electrons. The results verify the law $\nu = A(N - 7{\cdot}4)^2$, ν being the frequency, N the atomic number of the radiator, and A a constant. Plotting N against $\sqrt{\nu}$, all the rays of the series appear to lie on straight lines, but the homologous rays of the central part of the series are not similar in intensity. The intense rays for tungsten are numbers 4 and 6, and for iridium, platinum, and gold 4 and 5. W. G.

Quantitative Absorption Spectra. II. A New Ultra-violet Photometer. FREDERICK RUSSELL LANKSHEAR (*Mem. Manchester Phil. Soc.*, 1916, **60**, No. 10, 1—4. Compare A., 1915, ii, 605).—The photometer described is of the sector type, differing from previous instruments, however, in that the sector has a single semicircular aperture the diameter of which passes through the centre of the circular sector. By means of a disk with a corresponding aperture, which rotates on the face of the sector wheel, the aperture of the sector may be varied at will. H. M. D.

The Ultra-violet Transparency of certain Coloured Media. H. W. L. ABSALOM (*Phil. Mag.*, 1917, [vi], **33**, 450—455).—In the search for a substance opaque to the yellow region but transparent to the ultra-violet portion of the spectrum, the author has examined a number of coloured minerals and precious stones. Blue rock-salt from Stassfurt was found to transmit ultra-violet rays down to λ 2250, and the same degree of transparency was found for sylvite and for rock-salt and sylvite which had been coloured by the action of cathode rays.

Since the colour of blue rock-salt has been attributed to colloidal sodium, the investigation was extended to the blue solutions of metals in liquid ammonia. The most stable of these is the blue magnesium solution, which was found to transmit ultra-violet rays down to λ 2442. The limit of transmission for liquid ammonia is λ 2393.

These results would seem to show that ultra-violet transparency in a coloured mineral is favourable to the view that the colour is to be attributed to the presence of a colloidal metal. H. M. D.

Absorption of the Ultra-violet Rays by the Iodo-derivatives of Methane. G. MASSOL and A. FAUCON (*Compt. rend.*, 1917, **164**, 813—816).—Iodine in alcoholic solution shows three absorption bands, namely: (1) from $\lambda = 495$ to $\lambda = 420$ (max.

$\lambda=470$—465); (2) from $\lambda=389$ to $\lambda=339$ (max. $\lambda=355$); (3) from $\lambda=300$ to $\lambda=275$ (max. $\lambda=288$—287). The four iodo-derivatives of methane show the selective absorptive properties of iodine, but considerably modified, so that each derivative shows a particular spectrum. The first band of free iodine is not shown by any of the four iodo-derivatives of methane. The second band is shown by carbon tetraiodide and iodoform, but considerably broadened in the direction of increasing values of λ and with its maximum slightly displaced. The third band is found with carbon tetraiodide and iodoform slightly broadened towards the shorter wave-lengths, and in the case of di-iodomethane it occurs as a band stretching from $\lambda=330$ to $\lambda=262$, with a maximum at $\lambda=288$. With methyl iodide, a new band occurs at $\lambda=270$ to $\lambda=240$, having its maximum at $\lambda=250$. W. G.

Spectrographic Investigations of Azole Derivatives. I. Pyrazole and its Derivatives. N. A. Rozanov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1221—1250).—The author has investigated the absorption spectra of the following compounds: pyrazole, pyrazoline, 5-chloro-3-methylpyrazole, 3:5-dimethylpyrazole, 1:3:5-trimethylpyrazole, 3:4:5-trimethylpyrazole, 4-nitro-3:5-dimethylpyrazole, 1-phenylpyrazole, 3:5-diphenylpyrazole, 5-chloro-3-phenylpyrazole, 5-chloro-1-phenyl-3-methylpyrazole, 3-chloro-1-*o*-tolyl-5-methylpyrazole, 5-chloro-1-*o*-tolyl-3-methylpyrazole, 5-chloro-1-*o*-tolyl-3:4-dimethylpyrazole, pyrazolone, 3-methyl-5-pyrazolone, 3-phenyl-5-pyrazolone, 1-phenyl-5-pyrazolone, 3-chloro-1-phenyl-5-pyrazolone, 1-phenyl-3-methyl-5-pyrazolone, 1-*p*-tolyl-3-methyl-5-pyrazolone, 1-*o*–tolyl-3 : 4-dimethyl-5-pyrazolone, 1-phenyl-2 : 3-dimethyl-5-pyrazolone, 1-*o*-tolyl-3-methyl-5-pyrazolone, 3-hydroxy-1-phenyl-5-pyrazolone, 1-phenyl-5-methyl-3-pyrazolone, 1-*o*-tolyl-5-methyl-3-pyrazolone, 1-*p*-bromophenyl-5-methyl-3-pyrazolone, 1-*m*-nitrophenyl-5-methyl-3-pyrazolone, 4-nitro-1-*p*-nitrophenyl-3-methyl-5-pyrazolone, glyoxaline, and thiazole. From the results obtained, which are expressed as both curves and tables, the following conclusions are drawn.

The slight absorption of an open, saturated chain is changed very little by closure of the ring, the degree of absorption of pentane and *cyclo*pentane being one and the same. Introduction of an unsaturated nitrogen atom, and consequently of a double linking into the ring, intensifies the absorption. Hexane and *cyclo*hexane show weak absorption, *cyclo*hexene and *cyclo*hexadiene increasing general absorption, and benzene pronounced selective absorption with seven absorption bands. If selective absorption is explained as due to certain vibrations of the chemical molecule about a position of equilibrium, these occurring readily only with compounds of unsaturated character with an odd number of unsaturated groups (compare Baly and Collie, T., 1905, **87**, 1332), the introduction into the benzene nucleus of a new unsaturated group, such as the element nitrogen, should cause weakening of the oscillations and simultaneous diminution of the selective absorption; this is actually found to be the case, pyridine exhibiting only one absorption band. Contrary to expectation, introduction of a second nitrogen atom into the benzene nucleus does not enhance this effect, the intensity of the absorption bands with pyrazine being almost the same as with pyridine. It seems that, owing to the non-contiguity of the unsaturated elements, the vibrations of the molecule are not brought completely to a position of equilibrium, so that the selective absorption persists.

Confirmation of these relations is found with five-membered rings. Pyrrole exhibits greater absorption than *cyclo*pentane, and, as should be the case with a compound containing an odd number of unsaturated linkings, slight selective absorption. That introduction of a second nitrogen atom contiguous to the first into the pyrrole nucleus results in the annulment of the selective absorption is shown by the data for pyrazole and the simplest of its derivatives with saturated substituents. If, however, the second nitrogen atom introduced into the pyrrole is not adjacent to the first, the vibration should reappear, and, as is actually the case with glyoxaline, selective absorption be exhibited.

The results accompanying introduction of the unsaturated element sulphur into the glyoxaline molecule, and conversion of the latter into thiazole, which exhibits general absorption, are in contradiction to the above considerations, since, according to the latter, thiazole should exhibit selective absorption. Explanation of this point requires the investigation of a number of compounds of this type, including thiazole itself, of which the author had only a little at his disposal.

When the degree of unsaturation of pyrazole is diminished, as with pyrazoline, the extent of the absorption decreases. The unsaturated character of pyrazole compounds persists, however, on formation of salts, which give the same absorption curves as the corresponding bases, except for small alterations in the case of 5-chloro-3-phenylpyrazole. Introduction of auxochrome groups of the aliphatic series into the pyrazole nucleus results only in the displacement of the curves to the visible part of the spectrum, such displacement being most pronounced with the ortho-derivatives. If aromatic groups or the unsaturated nitro-group are inserted, absorption bands appear.

As regards oxygenated derivatives of pyrazole, pyrazolone gives an absorption band remaining constant on addition of alkali, so that only the ketonic grouping is to be attributed to it. If derivatives of pyrazolone do not give absorption bands, they must be regarded as derived from the iminic grouping of pyrazole. Hydroxy-derivatives of pyrazolone should react in two tautomeric forms, the ketonic and the enolic, and that this actually happens is shown by the alteration of the absorption curves on addition of alkali. Derivatives of 3-pyrazolone show curves very similar to that for 1-phenyl-2:3-dimethyl-5-pyrazolone (antipyrine), and should possess an iminic grouping, unalterable by alkali or acid; in general, these compounds absorb more strongly than the corresponding 5-pyrazolones.

The introduction of nitro-groups into the pyrazolone molecule causes marked change in the absorption curve, this being connected with tautomeric transformation of the pyrazolonic grouping, since the compounds obtained are capable of salt formation, this being exhibited clearly in the case of picrolonic acid.

The auxochrome theory of colour is confirmed in the derivatives of pyrazole. The groups :N·NH·, ·N:CH·NH·, and ·S·CH:N· are markedly chromophoric, the cause of this lying in the unsaturated nature, not only of the nitrogen itself, but of the whole group in general, since otherwise the formation of salts would exert an influence on the spectrographic curves. T. H. P.

Optical Activity of Proteins, Enzymes, Toxins, and Serums. M. A. Rakuzin (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1251—1294).—The author has collected from all sources data which have been obtained relative to the optical activity of animal and vegetable proteins and their derivatives, enzymes, toxins, and anti-serums. T. H. P.

Rate of Diffusion and Diameter of the Atom of Radium Emanation. Elisabeth Róna (*Zeitsch. physikal. Chem.*, 1917, **92**, 213—219).—The rate of diffusion of radium emanation in water, ethyl alcohol, benzene, and toluene is determined. From the diffusion constant D, the diameter S of the atom is calculated from the formula $S=RT/6\pi N\eta D$, in which N is the Avogadro constant $=6{\cdot}2\times10^{23}$ and η the viscosity of the solvent. The values thus obtained are 1·75, 0·63, 1·30, and $1{\cdot}24\times10^{-8}$ in water, ethyl alcohol, benzene, and toluene respectively. The differences between the several values are attributed to the lack of proportionality between the diffusion constant and the viscosity.

It is to be noted that the diffusion constants given by the author's measurements are very much larger than those previously obtained by Wallstabe (*Physikal. Zeitsch.*, 1903, **4**, 721). H. M. D.

Röntgen-investigation of Allotropic Forms. J. Olie, jun., and A. J. Byl (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 920—922).—According to Debye and Scherrer (*Physikal. Zeitsch.*, 1916, **17**, 277), secondary-ray interference figures are obtained when a finely divided, crystalline or quasi-amorphous substance in the form of a thin disk is subjected to the action of homogeneous *X*-rays. From the nature of the interference figure, conclusions may be drawn relative to the crystalline form of the substance in question.

The question of the behaviour of allotropic forms of the same substance has been examined by observations on the interference figures given by disks of compressed graphite and diamond powder. By the action of copper rays ($\lambda=1{\cdot}549\times10^{-8}$), interference figures of markedly different type were obtained with these two forms of carbon. H. M. D.

Kinetic Hypothesis to Explain the Function of Electrons in the Chemical Combination of Atoms. William A. Noyes (*J. Amer. Chem. Soc.*, 1917, **39**, 879—882).—A theoretical paper in which a brief review is given of the views held from the time of Berzelius down to the present day, of the connexion between electricity and matter. On the basis of the two generally held assumptions, the author puts forward an hypothesis to explain the function of the electron in chemical combination. On the assumptions (1) that the atoms are of a complex structure made up of positive nuclei and electrons, of which the latter are in rapid motion and have a velocity of about sixty times that of the hydrogen molecule, and (2) that the electrons are of two kinds in their relation to the structure of the atom, some of them being so involved in their orbits among the positive nuclei that they can never escape from the atom, and others, valency electrons, being transferable to other atoms, the author explains chemical combination in the following way. When two atoms, *A* and *B*, which have affinity for one another are brought together, a valency electron rotating round a positive nucleus in *A* may find a positive nucleus in *B* sufficiently close to include the latter in its orbit, and it may then continue to describe an orbit about both positive nuclei. During that portion of the orbit within *B*, *B* would become, on the whole, negative, whilst *A* would be positive. During the other part of the orbit, each atom would be electrically neutral, and the atoms might fall apart. Remembering the rapidity of the motion of the electron when compared with that of the atom, it appears that the motion of an electron in such an orbit might hold two atoms together. In ionisation, the electron would rotate about the nucleus of the negative atom, leaving the other atom positive. This hypothesis may be used to account for the localisation of the affinities in particular parts of the atoms, which is indicated by many organic compounds. J. F. S.

Electrical Conductivities of Dilute Sodium, Potassium, and Lithium Amalgams. Thomas B. Hine (*J. Amer. Chem. Soc.*, 1917, **39**, 882—895).—With the object of gaining an insight into the mechanism of the electrical conduction of metals, the author has determined the resistance of dilute amalgams of sodium, potassium, and lithium. The dilute amalgams were prepared from a concentrated amalgam of known composition in each case by adding measured volumes of mercury to it. The concentrated amalgams were prepared by the electrolysis of the alkali carbonates, using a pure mercury cathode. In the case of sodium, eleven different amalgams were measured, varying from 0·9 to 4·9 atoms %. The addition of sodium to mercury up to 2·40 atoms % increased the resistance, after which the value decreases again, and at 4·916 atoms % has practically reached the original mercury value. Seven determinations were made with lithium amalgams containing from 0·03 to 0·82 atom %; in this case the resistance decreases continuously with the addition of lithium. Seven determinations were also made with potassium amalgam containing from 0·058 to 1·186

atoms %. The resistance increases continuously with the addition of potassium. These results are considered from the point of view of the electron theory of conduction, and it is shown that the mechanism of conduction in the case of these amalgams is more complicated than that presented by the drift of free electrons due to an *E.M.F.* superimposed upon their disordered thermal motion.
J. F. S.

Conductivity Measurements on Oxidation-reduction Reactions. GRAHAM EDGAR (*J. Amer. Chem. Soc.*, 1917, **39**, 914—928).—Conductivity measurements have been made of solutions of ferrous sulphate which is being oxidised by the addition of potassium dichromate solution, and of potassium dichromate which is being reduced by the addition of ferrous sulphate. The measurements were made both in the presence of hydrochloric acid and sulphuric acid. In all cases reaction–conductivity curves are given, and the end-point of the reaction ascertained. In the oxidation of ferrous sulphate, it is shown that the curves are of the same general type as is observed in the neutralisation of an acid by a weak base, or of a base by a weak acid. The conductivity drops during the progress of the reaction, and then changes very little with an excess of dichromate. The conductivity may rise slightly, fall slightly, or remain constant after the end-point has been passed, depending on the acidity of the solution. The reason for the drop in the conductivity during the progress of the reaction is given by the equation

$$6Fe^{++} + Cr_2O_7^{=} + 14H^{+} = 6Fe^{+++} + 2Cr^{+++} + 7H_2O.$$

The concentration of the hydrogen ion falls during the reaction, and since the hydrogen ion in these strongly acid solutions carries most of the current, the conductivity must fall with it. After the end-point is reached, further addition of dichromate causes little change in the conductivity. The curves both before and after the end-point is reached are linear within the limits of experimental error. In the reverse action, that is, the reduction of potassium dichromate, the shape of the curve differs with different experimental conditions. If an acidified solution of potassium dichromate is titrated with ferrous sulphate to which no acid has been added, the curves are identical with those already described, but if to the ferrous sulphate such a quantity of acid has been added to make the solution of the same normality, both with regard to acid and ferrous iron, then the curve drops very slowly to the end-point and then rises steeply. A few preliminary results are given of the conductivity of ferrous sulphate solution which is being oxidised by potassium permanganate. On the whole, the conductivity reaction curves are the same as those obtained for dichromate, although the slope is not quite so great in this case. In these determinations, the permanganate must be added very slowly, particularly towards the end of the reaction. The influence of a number of factors on the conductivity reaction curves is discussed.
J. F. S.

Electrical Conductivity of Several Salts in Pyridine. J. Howard Mathews and Alfred J. Johnson (*J. Physical Chem.*, 1917, **21**, 294—310).—The electrical conductivity of lead nitrate, silver sulphate, copper acetate, silver thiocyanate, silver cyanide, and silver chloride has been determined at 25°, and in the first two cases at 0°, in pyridine solutions over a long range of concentration. The authors show that electrolytes fall into four classes: (1) those for which the equivalent conductivity curve rises rapidly in the more concentrated solutions and becomes asymptotic in the more dilute solutions; (2) those for which the conductivity increases more rapidly in the dilute solutions; (3) those which give minimum values for the equivalent conductivity; and (4) those which show an irregularity in their equivalent conductivity curves. The curves for silver sulphate, copper acetate, silver thiocyanate, and lead nitrate show an increase in the conductivity with increasing dilution without any indication of a maximum value being apparent. The curves for silver cyanide become almost parallel with the volume axis at intermediate dilutions, whilst silver chloride exhibits the same type of curve in a less marked degree. A résumé of the more recent hypotheses put forward to explain the anomalies found in electrical conductivity of salts in pyridine solution is given, and these hypotheses are discussed in the paper. J. F. S.

Potential of the Hydrogen Electrode at Different Pressures. N. E. Loomis, C. N. Myers, and S. F. Acree (*J. Physical Chem.*, 1917, **21**, 334—337).—The authors have undertaken the investigation of the hydrogen potential under different pressure conditions; in the present note they detail the various factors which have to be taken into account in the work. J. F. S.

Electromotive Forces and Electrode Potentials in Pure and Mixed Solvents. II. F. S. Mortimer and J. N. Pearce (*J. Physical Chem.*, 1917, **21**, 275—293. Compare A., 1915, ii, 7). —The electrode potentials $Ag|Ag^{\cdot}$ have been determined at 0° and 25° for solutions of silver nitrate in water, methyl alcohol, ethyl alcohol, pyridine, and binary mixtures of these solvents at a series of different concentrations. The dielectric constant has also been determined for the pure and mixed solvents. It is shown that the electrode potentials of silver are much higher for solutions in water and the two alcohols than for equivalent concentrations in pyridine. For any given concentration of silver nitrate, the *E.P.* increases with the decrease in the amount of pyridine present in the solvent. This increase is very gradual until 75% of the pyridine has been replaced by the second solvent. In the case of mixtures of pyridine with water or methyl alcohol, the dielectric constant increases, at first rather slowly with decrease in the percentage of pyridine, and then more rapidly with further decrease in the pyridine content. In all solvents, pure or mixed, the *E.P.* values increase with increasing concentration of the salt. The *E.M.F.* of all possible concentration cells in each of the pure and mixed solvents has been determined, and the values determined are shown to agree with those calculated from the *E.M.F.* values of solutions in the pure solvents in the case of water and the two alcohols; in the case of pyridine, however, the values calculated for the concentration cells from conductivity data do not even approximately agree with the experimentally determined *E.M.F.* values. Hence it is concluded that either the Nernst equation does not hold for concentration cells in pyridine or the electrical conductivity of these solutions is in no sense a measure of the degree of ionisation. The following values of the solution pressure of silver have been calculated from the experimental data: water, $2{\cdot}46 \times 10^{-17}$ atms.; ethyl alcohol, $2{\cdot}02 \times 10^{-18}$ atms.; methyl alcohol, $3{\cdot}55 \times 10^{-19}$ atms.; and pyridine, $1{\cdot}77 \times 10^{-10}$ atms. The heat of ionisation is calculated in the case of all solutions; for the pure solvents the following values are obtained: in water, 23,728 cal.; in pyridine, 3726 cal.; in ethyl alcohol, 21,472 cal.; and in methyl alcohol, 22,400 cal. The following dielectric constants have been obtained: water, 80·5; 75% water, 25% pyridine, 56·9; 50% water, 50% pyridine, 41·1; 25% water, 75% pyridine, 31·5; pyridine, 11·2; methyl alcohol, 32·8; 75% methyl alcohol, 25% pyridine, 24·5; 50% methyl alcohol, 50% pyridine, 18·2.

J. F. S.

The Theory of Overvoltage. EDGAR NEWBERY (*Mem. Manchester Phil. Soc.*, 1916, **60**, No. 11, 1—34. Compare T., 1914, **105**, 2434; 1916, **109**, 1051, 1066, 1107).—An account is given of the phenomena of overvoltage, the factors on which it depends, the methods of measuring the effect, and the theories which have been put forward to account for overvoltage.

None of these theories is in agreement with all the facts at present known, and a new theory is suggested which includes certain ideas involved in the older theories of Nernst, Le Blanc, and Foerster. According to this, the overvoltage effect at the surface of a metal is determined by four factors, defined as (1) supersaturation of the metal surface with gas in consequence of the permeability of the metal to the ionised gas and its impermeability to non-electrified gas molecules, and, further, of the spontaneous decomposition of the alloys which are formed by the metal and the gas in question; (2) formation of alloys or solid solutions at the electrode surface; (3) relative concentration of non-hydrated ions, charged and discharged, at the metal surface; (4) inductive action of the escaping ionised gas on the electrode. H. M. D.

[The Passive Condition of Metals.] J. STAPENHORST (*Zeitsch. physikal. Chem.*, 1917, **92**, 238—254).—In explanation of the relation between the active and passive states of a metal, it has been suggested that hydrogen and oxygen act as catalysts in promoting the transformation of one form of the metal into the other. A number of experiments are described in which the author seeks to distinguish between the hydrogen and oxygen theories as applicable to certain metals which show the phenomenon in question.

Iron which has been rendered passive by the action of chromic acid becomes active under the influence of hydrogen dissolved in the metal. In this experiment, the hydrogen was generated electrolytically on the opposite side of a thin iron plate, the hydrogen diffusing through the plate to the surface in contact with the chromic acid solution. It is shown that this change cannot be explained by the removal of dissolved oxygen or by the destruction of an oxide film. Under suitable conditions, the reverse change may be brought about by the diffusion of nascent oxygen.

The potential assumed by a metal in a neutral electrolyte depends on the quantity of oxygen present in the electrolyte solution. If the surface of the metal is renewed by grinding with an emery-wheel, the potential changes from that characteristic of the passive form to the value peculiar to the active form of the metal. Hydrogen and nitrogen tend to preserve the potential of the active form, but otherwise behave as indifferent gases. Oxygen, on the other hand, is not an indifferent gas. Both in the gaseous and dissolved states it exercises a very considerable influence on the electrode potential and conduces to the appearance and maintenance of the passive condition. H. M. D.

The Concentration of the Electrolytes in the Neighbourhood of the Electrodes. ST. PROCOPIU (*Compt. rend.*, 1917, **164**, 725—727).—It has previously been shown that in addition to the Helmholtz-Lippmann double layer round the electrode, there is another layer of electrolyte of concentration different from that of the mass of liquid (compare A., 1915, ii, 816). A formula is now given for determining the thickness of this layer, namely, $x_1 = x_0 e^{kv/v}$, where x_1 is the thickness of this layer, x_0 is the thickness of the double layer, k the dielectric constant of the solvent, ν the *E.M.F.* produced by displacement of the electrode, and v is the potential, metal–liquid. A comparative idea of the thickness of this second layer is obtained by determining how soon the *E.M.F.*, produced by the movement of the electrode, disappears.
W. G.

Examples of Electrolysis with Alternating Current. A. RÍUS Y MIRÓ (*Anal. Fis. Quim.*, 1917, **15**, 182—191).—An account of electrolyses carried out with alternating currents of different frequencies in dilute solutions of sulphuric acid, hydrochloric acid, and sodium hydroxide, electrodes of copper, iron, and aluminium being employed. A. J. W.

The Electro-capillary Function. G. GOUY (*Ann. Physique*, 1917, [ix], **7**, 129—184).—A theoretical discussion of results previously published (compare A., 1906, ii, 652, 725; 1908, ii, 654; 1916, ii, 550). W. G.

The Cooling of Different Metals by Immersion in Water. GARVIN and A. PORTEVIN (*Compt. rend.*, 1917, **164**, 783—786).—A study of the cooling curves of silver, aluminium, nickel, and a nickel-steel containing 30% of nickel, the metals being used in the form of homothetic cylinders, the diameter varying between 8 mm. and 20 mm. and the length equal to 3*d*., the metals being tempered in a current of water at high temperatures. The work was carried out under the conditions formulated by Le Chatelier (compare *Rev. de Métallurgie*, 1904, **1**, 475) and realised by Benedicks (compare *J. Iron Steel Inst.*, 1908, 153). The results and curves, which will be published in another communication, show that concordant curves are obtained for the samples which cool slowly, but for the others considerable variation is found. The curves show a point of inflexion corresponding with the commencement of tempering. Beyond this point the curves do not appear to obey a mathematical law, as suggested by MacCance (compare *J. Iron Steel Inst.*, 1914, **89**, 192). The velocity of cooling increases slightly when the temperature of tempering is raised.

W. G.

Cooling Curves of Ternary and Quaternary Mixtures. N. PARRAVANO and C. MAZZETTI (*Gazzetta*, 1917, **47**, i, 133—143).—Cooling curves of mixtures often fail to present distinctly the discontinuities which are characteristic of them, and are utilised for constructing diagrams of state. Of the various causes contributing to this failure, the form of the melting-point diagram of the series to which a mixture belongs and the position of the mixture in this series have been insufficiently considered. Hanemann (A., 1915, ii, 413) has, however, shown that, with binary mixtures it is possible generally to establish the influence exerted on the form assumed by the cooling curves by the form of the diagram and the position of the mixture in it. The authors now indicate, with the help of figures, how the form which may be expected for the cooling curves of ternary and quaternary mixtures may be established when the diagram of state is known; in some cases the deductions usually drawn from the discontinuities observed in the cooling curves are found to be inaccurate.

T. H. P.

A Statistical Study of Organic Series. W. E. FORBES (*Chem. News*, 1917, **115**, 229).—By comparing the so-called coefficients of variation of the boiling point for various homologous series it is found that the value for the paraffin hydrocarbons is much greater than the values for the alcohols, fatty acids, and the benzene series of hydrocarbons. The difference shown by the paraffin and the benzene series of hydrocarbons is supposed to be connected with the structure of the benzene nucleus. H. M. D.

Heat of Formation of Ferrous Sulphide. N. PARRAVANO and P. DE CESARIS (*Gazzetta*, 1917, **47**, i, 144—149).—The authors have determined the heat of formation of ferrous sulphide calorimetrically, the reaction between finely divided reduced iron and sulphur being initiated by a platinum wire electrically heated. The number of cals. generated per 1 gram of ferrous sulphide varied from 258·2 to 266·0, the mean being 262·4 and the molecular heat 23,070 cals. For the precipitated sulphide, Berthelot found 24,000 and Thomsen 23,780 cals.

Neglecting the small thermal change accompanying the polymorphic transformation of ferrous sulphide at 298°, the dissociation pressures for ferrous sulphide and manganese sulphide are calculated from the Nernst formula, $\log p = -Q/4\cdot571T + 1\cdot75 \log T + 3$, for the temperatures 800°, 900°, 1000°, and 1100°, the values for the latter being much smaller than those for the former at the same temperature. Consequently, the reaction $FeS + Mn = MnS + Fe$ should take place, as is indeed known to be the case. T. H. P.

Molecular Condition of Pure Liquids. II. P. N. Pavlov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1175—1196. Compare this vol., ii, 125).—The considerations previously developed show that Kistiakovski's rule (A., 1906, ii, 655; 1913, ii, 837) is quite inapplicable to the investigation of the molecular constitution of liquids.

A number of further conclusions are deduced, the principal ones being as follows. The molecular volumes of normal liquids at corresponding temperatures (in corresponding states) are equal. Equal volumes of normal liquids at identical reduced temperatures and pressures contain equal numbers of molecules. Further, normal liquids and their saturated vapours under corresponding conditions possess those structural peculiarities which Avogadro discovered for gases (ideal) at identical absolute temperatures and pressures. The true molecular volumes of all liquids (normal and abnormal) at corresponding temperatures and under the pressure of their saturated vapours are equal.

The ratio, $V_1 : V$, of the molecular volume of an abnormal liquid to that of a normal liquid at the corresponding temperature is termed the abnormality number, N, and abnormal liquids are associated or dissociated according as N is less than or greater than unity. In investigating the molecular volumes of liquids, these are compared with the values for carbon tetrachloride at the corresponding temperatures, and use is made of functions of the form $\gamma v^n/T$ or of some other function containing γ.

The values of N have been calculated, and are tabulated, for 108 elements and compounds, of which only four, namely, carbon tetrachloride, ether, ethyl acetate, and propyl formate, exhibit normal molecular volumes. The data for homologous series show that the accumulation of mass in a molecule diminishes the association and increases the dissociation of liquids. Thus, methane is strongly associated, *n*-pentane dissociated, *n*-hexane more dissociated, and *n*-heptane still more dissociated. Further, benzene is associated, toluene dissociated, xylene more dissociated, and mesitylene and durene still more dissociated. A similar relation holds for the series water, methyl, ethyl, propyl, butyl, and *iso*amyl alcohols, for the series of carboxylic acids, esters, etc., and for such series as benzene, fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene. Marked association is exhibited by the elements in the liquid condition. T. H. P.

Comparative Adsorption of Sucrose, Inulin, and Dextrin. M. A. Rakuzin (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1319—1324).—The author's previous work indicates that the necessary conditions for every adsorption include the colloidal state of the adsorbed substance and adsorbent, the only case observed in which a crystalline substance is irreversibly adsorbed by a colloidal adsorbent being that of the solid paraffins of naphtha by aluminium hydroxide, floridin, etc.

In order to test the accuracy of Freundlich's rule, that adsorption is prevented by a tendency to dissociation and by an accumulation of hydroxyl groups, the author has now carried out experiments on the adsorption of sucrose, inulin, and dextrin. The results show that this rule holds only for crystalline carbohydrates, such as sucrose and inulin; colloidal carbohydrates, on the other hand, are well adsorbed by both aluminium hydroxide and animal charcoal, and in the case of dextrin (commercial "dextrinum purissimum") both these adsorptions are irreversible with respect to boiling water. Further, both adsorptions are quantitative; animal charcoal adsorbs 8·04% of β-achroodextrin and aluminium hydroxide 16·02% of products intermediate to β- and γ-dextrins. The above commercial dextrin is found to be a mixture of maltodextrin with β-achroodextrin and products intermediate to β- and γ-achroodextrins. T. H. P.

The Osmotic-Kinetic Theory of Dilute Solutions. Karl Jellinek (*Zeitsch. physikal. Chem.*, 1917, **92**, 169—212).—A theoretical paper in which the osmotic theory of solutions is examined from the kinetic point of view. It is shown that the van der Waals's equation may be employed in the derivation of the relation between the osmotic pressure, the concentration, and the temperature and of the laws regulating the lowering of the vapour pressure and the freezing point and the raising of the boiling point. The assumptions made in the theoretical treatment are (1) additivity of the volumes of solvent and solute, (2) additivity of the volume correction factor b. H. M. D.

Calculation of the Coefficient of Diffusion of a Salt at a Definite Concentration. A. Griffiths (*Proc. Physical Soc.*, 1917, **29**, 159—162).—It is shown that the coefficient of diffusion may be calculated without a knowledge of the exact relation between the density and the concentration of the solution. The method of calculation adopted by Clack (compare A., 1915, ii, 45) is thereby justified. H. M. D.

Osmotic Pressure: its Relation to the Membrane, the Solvent, and the Solute. Frank Tinker (*Phil. Mag.*, 1917, [vi], **33**, 428—450).—A theoretical paper in which the author discusses the relation of osmotic pressure to the solvent, the solution, and the semipermeable membrane. It is assumed that the pressure of each component in the interior of a fluid mixture is inversely proportional to the free space available to the molecules, and that the exact relation between the partial pressure of the component and the free space per molecule is given by the equation–partial pressure × available free space per molecule of the component $=RT$. Dissociation and association of the solute and solvent and combination between them are also supposed to be excluded.

By making use of the Dieterici equation of state it is shown that two ideal solutions of equal molar concentration are in osmotic equilibrium, that this equilibrium does not obtain if one solution is ideal and the other not, although the solutions may be equally concentrated, and that osmotic equilibrium between non-ideal solutions is possible only when the solutions have equal heats of dilution.

The general equation connecting the osmotic pressure with the vapour pressures of solvent and solution, both supposed to be at atmospheric pressure, reduces for dilute solutions to the form $PV=RT+q$, in which V is the volume of solution containing 1 mol. of solute and q is a measure of the heat change on dilution. This equation has already been given by Bancroft (A., 1906, ii, 523). It follows that the osmotic pressure of a dilute solution is given by the simple gas equation only when the solution has zero heat of dilution. If the heat of dilution is positive, the osmotic pressure is abnormally high, whilst if the heat of dilution is negative the osmotic pressure is abnormally low.

Consideration of the compressibility relationships shows that the free space within a dilute solution having zero heat of dilution is equal to $RT\beta$, where β is the coefficient of compressibility. Since the pure solvent is the limiting case of a dilute solution, this relation must hold for pure liquids. H. M. D.

Pervaporation, Perstillation, and Percrystallisation. PHILIP ADOLPH KOBER (*J. Amer. Chem. Soc.*, 1917, **39**, 944—948).—Collodion and parchment membrane containers permit water to evaporate through the walls as though no membrane were present. This phenomenon is termed pervaporation. Distillation by means of pervaporation is termed perstillation, and can be carried out at ordinary pressures with low temperatures, as well as in a vacuum. When a dialysable constituent of a liquid within these containers reaches saturation, crystallisation usually takes place on the outside of the container; this is termed percrystallisation. A number of experiments are described to show the nature of these phenomena; thus it is shown that in twenty-four hours 325 c.c. of a solution containing serum albumin and 25 c.c. of toluene had lost all its water at 37° when closed in a collodion container. Also pervaporation occurs so rapidly when water is placed in a closed collodion vessel and heated by a Bunsen flame that the liquid sinks in the vessel perceptibly, like a slowly emptying burette. It is also shown that it is not possible to raise the temperature of water in such a container above 92° when a Bunsen is used as the source of heat. The cause of these phenomena is discussed and tentative hypotheses are put forward to explain them. J. F. S.

Crystal Structure and Chemical Valency. J. Beckenkamp (*Centr. Min.*, 1917, 97—110).—If the Sohncke theory of point systems be rigidly applied to crystals, the conceptions of molecule and valency in such structures become meaningless. In the structures put forward by W. H. and W. L. Bragg for rock-salt and sylvine, the atoms of the two kinds form an interpenetrating point system, and no molecules are distinguishable. The author shows that in the structures which he has already put forward for various minerals, for example, for quartz, the individuality of the molecule is preserved. The author supposes the distances between atoms in the structure to be determined by the positions of nodes formed by the interference of radiation waves from the respective atoms, the wave-lengths being a function of the atomic weights. He concludes, from the relative atomic weights of sodium and chlorine, that the ultimate structure of a crystal of rock-salt has a triclinic character, but that by a species of submicroscopic twinning a pseudo-regular structure is built up indistinguishable from a truly cubic one. The Bragg structure gives merely the average position of the atoms.

A similar conclusion has been reached by J. Stark (*Jahrb. Radioaktiv. Elektronik*, 1915, **12**, 280) from considerations of electro-affinity. He considers it impossible that intramolecular linkings can be destroyed in the crystal, but finds that in a structure of sodium and chlorine ions (rock-salt) there will be formed complexes having an axis of hemimorphous tetragonal symmetry. By the twinning of such complexes, a quasi-homogeneous mass having holohedral cubic symmetry results. E. H. R.

Results of Crystal Analysis. IV. The Structure of Ammonium Iodide, Tetramethylammonium Iodide, and Xenotime. L. Vegard (*Phil. Mag.*, 1917, [vi], **33**, 395—428. Compare A., 1916, ii, 405, 593).—The results obtained in the *X*-ray spectroscopic examination of crystals of ammonium and tetramethylammonium iodides indicate that the existence of a simple relation between the topic parameters does not necessarily involve any very simple relation between the lattices. It is shown that the morphotropic relationship cannot be explained by replacement of the hydrogen atoms in ammonium iodide by tetragonally arranged carbon atoms. The observations show, in fact, that the iodine and nitrogen lattices are not only quite differently arranged, but that the elementary lattice of tetramethylammonium iodide contains two molecules, whilst that of ammonium iodide contains four molecules.

Further investigation of the structure of xenotime has shown that the atoms of xenotime are arranged in a lattice of the zircon type, and the previously expressed opinion (compare *loc. cit.*) that the lattice systems are of different type can no longer be maintained. The conception of xenotime as a phosphate, YPO_4, is accordingly not in accordance with the crystalline structure, which suggests that the constitution of the substance in the crystalline form is that represented by YO_2PO_2. H. M. D.

Mixed Crystals. Carlo Viola (*Atti. R. Accad. Lincei*, 1917, [v], **26**, i, 195—207. Compare this vol., ii, 79, 80).—The author now proceeds to examine the equilibrium contact conditions between a mixed crystal and the amorphous phase from which it originates. This problem is solvable by means of the data required to prove Curie's law, according to which the growths perpendicular to the faces of a crystal are directly proportional to their respective capillary constants.

The mixed crystal is composed of two constituents, that is, of two crystals in intimate contact in their smallest parts. It will be in equilibrium with the amorphous phase, which contains the same constituents, but usually in different proportions, when (1) the proportion between the two components does not alter, although the total mass changes in correspondence with Gibbs's phase rule, (2) when the surface energy is a minimum in correspondence with the least action, and (3) when the total volume of the mixed crystal does not vary, the only possible variation being in the form.

It is shown analytically that the mean growths perpendicular to the faces of the mixed crystal are directly proportional to the mean capillary constants of the two components. From this it follows that the normal figure of a mixed crystal is the mean of the normal figures of the crystals composing it in the proportions in which these are found in the mixed crystal. It is shown further that the total surface energy is always directly proportional to the total volume of the mixed crystal, this being Curie's law, and that the difference in the surface energies of the components is directly proportional to the difference in the volumes at every instant of the growth, no matter what the relation between the components of the mixed crystal. Isomorphous crystals are defined as those having the same structure and the same surface density, and therefore exhibiting continuous miscibility between limits which include the mean miscibility. Various examples are considered in order to illustrate the significance of the inclusion in the above definition of the idea of mean miscibility.

T. H. P.

Mathematical Theory of the Kinetics of the Coagulation of Colloidal Solutions. M. von Smoluchowski (*Zeitsch. physikal. Chem.*, 1917, **92**, 129—168).—Inductive methods applied to the available data on the kinetics of coagulation processes have not led to any satisfactory theory of the coagulation process, and this is largely attributed to the circumstance that the properties of the colloidal solutions which have been investigated in this connexion do not afford a satisfactory indication of the progress of the coagulation.

An attempt is made to build up a theory of the phenomenon by deductive methods. It is assumed that the colloidal particles attract one another in virtue of capillary forces when the distance between them is sufficiently small. That this attraction does not lead to combination in normal circumstances is due to the protective action of the electrical double layer surrounding the particles. On the addition of an electrolyte, ion adsorption occurs and the double layer is partly or completely eliminated, with the result that the colloidal particles combine to form larger aggregates under the influence of the capillary forces. The Brownian motion of the particles only comes into play as a factor in coagulation in so far as it facilitates the approximation of the particles, and thus indirectly affects the operation of the capillary and electric forces.

Formulæ are derived for the course of an ideal coagulation which are found to be in satisfactory agreement with previous observations on the kinetics of coagulation processes. In regard to the influence of the concentration of the colloid on the rate of coagulation, these formulæ are comparable with equations for ordinary chemical reactions of the second order.

Rapid coagulation processes and chemical reactions may be regarded as opposite and extreme cases of the ideal coagulation processes which are more particularly considered in connexion with the author's theory. Whilst the former can be regarded as determined solely by diffusion factors, it would seem that ordinary chemical reactions involve some unknown factor, the effect of which is to reduce the number of collisions which result in chemical interchange to a very small fraction of the total number of the molecular collisions. H. M. D.

Protective Colloids. VIII. Tubera Salep as Protective Colloid. 2. Colloidal Silver. A. GUTBIER and NORA KRÄUTLE (*Kolloid Zeitsch.*, 1917, **20**, 123—127. Compare this vol., ii, 244).—The preparation of colloidal solutions of silver by the action of sodium hyposulphite in presence of extract of *Tubera Salep* as protective colloid is described in detail. The silver sols thus obtained are of great stability, and this stability does not seem to be affected by the fact that the colour of the solutions in transmitted light varies with the conditions. H. M. D.

Protective Colloids. VIII. Tubera Salep as Protective Colloid. 3. Colloidal Arsenic. A. GUTBIER and NORA KRÄUTLE (*Kolloid Zeitsch.*, 1917, **20**, 186—194).—Experiments are described in which the authors have examined the protective action of extracts of various plant colloids on colloidal arsenic prepared by the reducing action of sodium hyposulphite on slightly acidified solutions of arsenious oxide. The protective action is very marked, and it has been found possible to obtain by evaporation solid colloids containing about 3% of arsenic which are completely soluble in water.

According to observations on the colour, the protected solutions of colloidal arsenic are not appreciably influenced by the addition of hydrochloric acid, sulphuric acid, sodium chloride, and barium chloride, whereas sodium hydroxide and sodium carbonate change the colour from dark brown to light yellow. H. M. D.

Protective Colloids. VIII. Tubera Salep as Protective Colloid. 4. Colloidal Antimony. A. Gutbier and Nora Kräutle (*Kolloid Zeitsch.*, 1917, **20**, 194—198).—Colloidal solutions of antimony, prepared by the action of sodium hyposulphite on a solution of potassium antimoniate acidified slightly by the addition of tartaric acid, are found to have their stability considerably increased in presence of the extract of *Tubera Salep.* The dialysed solutions may be evaporated to give solid colloids containing about 10% of antimony which dissolve completely in water. The stability of the protected solutions is not affected by the addition of acids and neutral salts, but alkalinity reduces the stability to a large extent. In this respect, the behaviour of the colloidal antimony solutions resembles that of solutions of the protective colloid. H. M. D.

The Use of Citarin in Scientific Chemistry. L. Vanino (*Kolloid Zeitsch.*, 1917, **20**, 122).—The addition of small quantities of the sodium salt of anhydromethylenecitric acid ("citarin") to solutions of gold, silver, and other metallic salts results in the formation of colloidal solutions of the respective metals. The colloidal gold solutions are red in colour, although violet-blue solutions are usually obtained by the action of other reducing agents. H. M. D.

Theory of Emulsification based on Pharmaceutical Practice. Leo Roon and Ralph E. Oesper (*J. Ind. Eng. Chem.*, 1917, **9**, 156—161).—The authors review briefly the theories of emulsification which have been advanced, and the methods employed in pharmaceutical practice for the preparation of emulsions. The present work was confined to the study of acacia and soap emulsions, and reveals the existence of definite critical points of emulsification, depending on the quantities of internal phase and of emulsifier, the nature of these two factors, and the procedure followed in the preparation of the emulsion. The results, in agreement with Fischer's theory, indicate that the presence of a hydration compound of the nature of a hydrated colloid is necessary for emulsification, and that the best emulsion is produced when this hydration compound is formed at the moment of dispersion of the internal phase; in other words, emulsifier, water, and oil in critical proportions must all be mixed together at once in order to form a properly hydrated nucleus, which may then be diluted. This is in accord with the usual pharmaceutical practice. No emulsion results if the emulsifier (gum acacia or soap) is diluted before the dispersion of the internal phase. Emulsion nuclei of one composition act as stabilisers or emulsifiers respectively for incomplete emulsions of other compositions, or for other internal phases. G. F. M.

In-, Uni-, and Bi-variant Equilibria. XIV. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 927—932. Compare this vol., ii, 195).—A discussion of the relations exhibited by systems in which three indifferent phases co-exist. H. M. D.

Equilibrium in the System: Mercuric Iodide-Pyridine. J. Howard Mathews and Philip A. Ritter (*J. Physical Chem.*, 1917, **21**, 269—274).—The solubility of mercuric iodide has been determined in pyridine at temperatures between $-50°$ and $+98·5°$. Over this range of temperature the solubility changes regularly from 1·95% mercuric iodide in the solution to 65·30%. It is shown that the saturated solution at all temperatures is in equilibrium with the compound $HgI_2,2C_5H_5N$, and this is the only compound which exists between these limits. It crystallises, however, either in long, monoclinic needles or in short, monoclinic prisms, but there appears to be no definite transition point between the two forms.

J. F. S.

Velocity of Reaction in Heterogeneous Systems and Size of Granules. Emil Podszus (*Zeitsch. physikal. Chem.*, 1917 **92**, 227—237).—It has been found that certain oxides, which in ordinary circumstances are unacted on by hydrochloric acid, are dissolved by this reagent to a very appreciable extent when the oxides are reduced to a fine state of subdivision. The experiments were made with aluminium oxide, thorium oxide, and zirconium oxide, and in each case the oxide is dissolved when the diameter of the particles is of the order 1 μ. The results recorded show the progress of the dissolution when the concentration of the acid and the temperature are kept constant, and, further, the influence of variation in the acid concentration. It would seem that oxides which are apparently insoluble in acids may be dissolved provided the size of the particles is sufficiently reduced.

The observations cannot be explained in terms of the diffusion theory, and in consideration of the small size of the particles it is not surprising that the behaviour should deviate from that which has been found associated with reactions in heterogeneous systems. Although the size of the particles of a substance is known to have a considerable influence on many of its properties, including the solubility, it does not seem possible to account for the observed facts on this basis. H. M. D.

The Influence of Pressure on the Ignition of a Mixture of Methane and Air by the Impulsive Electrical Discharge. Richard Vernon Wheeler (T., 1917, **111**, 411—413. Compare *ibid.*, 130).—Further experiments on the influence of pressure on the energy of the igniting current have been made at pressures greater than atmospheric. No evidence of "stepped ignition" is shown by the results obtained at pressures varying from 500 to 5000 mm., the curve obtained by plotting the igniting current against the pressure of the gaseous mixture being perfectly continuous.

When a spark-gap of 1 mm. was employed at pressures somewhat higher than atmospheric, it was found that the least discharge which could cross the gap caused ignition of the mixture. By using a smaller spark gap (0·25—0·5 mm.), however, it was possible to make the observations required. This factor offers a possible explanation of the divergent results obtained by Thornton (compare A., 1914, ii, 834), the suggestion being that his data disclose merely the influence of the pressure on the facility with which the discharge passes across the spark gap. H. M. D.

Velocity of Decomposition and the Dissociation Constant of Nitrous Acid. PRAFULLA CHANDRA RÂY, MANIK LAL DEY, and JNANENDRA CHANDRA GHOSH (T., 1917, **111**, 413—417).—Solutions of nitrous acid are readily obtained by the interaction of equivalent solutions of barium nitrite and sulphuric acid. Measurements of the rate of decomposition of nitrous acid solutions show that the reaction proceeds in accordance with the equation for a unimolecular change, the velocity-coefficients at 0°, 21°, and 40° being 0·00014, 0·00022, and 0·00057 respectively. According to conductivity data, the ionisation constant of the acid at 0° is $6{\cdot}0 \times 10^{-4}$.

The most concentrated solution of nitrous acid which could be obtained at 0° by the above method was 0·185*N*. H. M. D.

Reduction of Mercuric Compounds. G. A. LINHART and E. Q. ADAMS (*J. Amer. Chem. Soc.*, 1917, **39**, 948—950).—In previous papers Linhart has shown that the velocity of the reduction of mercuric chloride by phosphorous acid and by sodium formate follows the equation for a reaction of the second order, and not that of a reaction of the third order (A., 1913, ii, 490; 1915, ii, 91). In the present paper it is shown that the reduction of mercuric compounds may be represented as going first directly to mercury or some substance which behaves like mercury, and then, if conditions permit, to mercurous compounds. This manner of representation accounts for the fact that the reaction is bimolecular, so far as concerns the kinetics of the reaction, and it removes the necessity for specific explanations for each reducing agent.

J. F. S.

Studies on the Walden Inversion. V. The Kinetics and Dissociation Constant of α-Bromo-β-phenylpropionic Acid. GEORGE SENTER and GERALD HARGRAVE MARTIN (T., 1917, **111**, 447—457).—According to conductivity measurements at 25°, the ionisation constant of α-bromo-β-phenylpropionic acid is 0·00172. The limiting conductivity of the sodium salt is $\Lambda_\infty = 79{\cdot}0$, from which the mobility of the anion is 28 and λ_∞ for the acid 375.

The kinetics of the displacement of bromine by hydroxyl have been investigated according to methods described previously (compare T., 1915, **107**, 908; 1916, **109**, 690). Both the free bromo-substituted acid and its sodium salt give at 50° almost exclusively the corresponding hydroxy-acid, but in presence of sodium hydroxide this reaction is accompanied by the formation of a considerable proportion of cinnamic acid as a result of the elimination of hydrogen bromide from the bromophenylpropionic acid.

Comparison of the velocity-coefficients obtained in experiments with solutions containing (1) the free acid, (2) its sodium salt, (3) the free acid with the addition of nitric or benzenesulphonic acid, shows that the reaction measured is the action of water on the $CH_2Ph\cdot CHBr\cdot CO_2'$ ion. The non-ionised acid reacts with water much less rapidly at 50°.

The temperature-coefficient of the reaction is probably the highest yet observed for a pseudo-unimolecular reaction, the velocity becoming 4·6 times as great when the temperature is increased by 10°.

When the data for α-bromo-β-phenylpropionic acid are compared with results obtained for α-bromopropionic acid, it is found that the bromine is acted on less rapidly in the first-mentioned acid. This is not in accord with previous observations relative to the influence of the phenyl group in such reactions. H. M. D.

A New Method for the Measurement of the Velocity of Crystallisation of the Metals. J. Czochralski (*Zeitsch. physikal. Chem.*, 1917, **92**, 219—221).—The method depends on the determination of the maximum velocity with which a thin, crystalline thread of the metal may be drawn continuously from a bath of the liquid metal. The maximum velocities found for tin, lead, and zinc at their respective melting points were respectively about 90, 140, and 100 millimetres per minute. H. M. D.

Studies in Catalysis. VI. The Mutual Influence of Two Reactions proceeding in the same Medium. Robert Owen Griffith, Alfred Lamble, and William Cudmore McCullagh Lewis (T., 1917, **111**, 389—395).—In view of the disagreement between the results obtained by previous observers, further investigation has been made of the change in the velocity-coefficients of the inversion of sucrose and the hydrolysis of methyl acetate when the two reactions take place in the same solution. In presence of methyl acetate, the rate of inversion of sucrose is at first slightly diminished. With increasing ester concentration the velocity-coefficient passes through a minimum value, the subsequent increase being attributed to the diminution in the negative catalytic effect of water which is displaced on addition of the ester.

The presence of sucrose increases the rate of hydrolysis of methyl acetate, but when a correction is made for the influence of the displaced water, it appears that sucrose is a feeble negative catalyst. H. M. D.

Studies in Catalysis. VII. Heat of Reaction, Equilibrium Constant, and Allied Quantities from the Point of View of the Radiation Hypothesis. William Cudmore McCullagh Lewis (T., 1917, **111**, 457—469. Compare T., 1916, **109**, 796).—The idea that molecules become reactive when the energy content reaches a certain critical value is shown to be quite compatible with the fact that the reaction involved may be exothermic or endothermic. By considering the case of a unimolecular reversible reaction, it is shown that the heat of the reaction at constant volume, Q_v, is connected with the critical increments of the two kinds of molecules by the equation $+Q_v = E_2 - E_1$. By introduction of the quantum hypothesis, this assumes the form $-Q_v = Nh(\nu_1 - \nu_2)$, in which N is the Avogadro constant, h Planck's constant, and ν_1 and ν_2 the critical frequencies of the reacting and resulting molecules. This relation has been previously derived by Haber from the consideration of a somewhat special case.

From a consideration of the magnitude of the heat effects accompanying chemical reactions, it is shown that the mean internal energy of the molecules is in many cases much greater than can be accounted for by the temperature, and the conclusion is drawn that the energy content is large even at absolute zero. The temperature at which an uncatalysed reaction first proceeds with measurable velocity gives some idea of the magnitude of the energy quantum which is required to bring the molecules of a substance into the reactive condition.

The radiation hypothesis is applied to bimolecular reactions, and expressions are derived for the velocity-coefficient and the influence of temperature on the velocity. It is inferred that the higher the order of a reaction, the greater is the probable value of its temperature-coefficient.

Formation of intermediate compounds will have an influence on the magnitude of the velocity-coefficient, but the rate of change of this with temperature will not be affected if catalytic influences are excluded. H. M. D.

Evolution of the Elements and the Stability of Complex Atoms. A New Periodic System which shows a Relation between the Abundance of the Elements and the Structure of the Nuclei of Atoms. WILLIAM D. HARKINS (*J. Amer. Chem. Soc.*, 1917, **39**, 856—879).—A theoretical paper. In previous papers (A., 1916, ii, 240) it is shown that elements are very probably interatomic compounds of hydrogen, and that one of the first steps in the formation of a complex atom is the change of hydrogen into helium. On this hypothesis, the elements are found to fall into two series: the series of even atomic number, beginning with helium and having the general formula $n\mathrm{He}'$, and the series of elements with odd atomic numbers, beginning with lithium and having the general formula $n\mathrm{He}' + \mathrm{H}'_3$. If the elements actually belong to these two series, as the hypothesis indicates, it is to be expected that the properties of the elements of the two series should indicate the differences between them. This has been shown, from the interpretation of the atomic weights in the light of the disintegration of the radioactive elements, to be the case, and consequently evidence of the validity of the present hypothesis is thus furnished. Further evidence is now put forward which is in complete accord with the system. The ordinary periodic system of the elements seems to be a relationship which expresses in a graphic way the variations in the arrangement and the number of the external electrons, especially the valency electrons, in the atom, which finds its expression in the chemical and physical properties of the elements. The hydrogen–helium system is most fundamentally related to the structure of the nuclei of the atoms, and this structure should not affect the arrangement of the external electrons if the nucleus is extremely minute, since this arrangement would depend on the number of electrons, which in turn depends on the nuclear charge, but not on the internal structure of the nucleus except in so far as this structure affects the total charge. The structure of the nucleus should, however, affect its stability, which would have an expression in the abundance of the respective elements. There is another factor, too, which would have an effect on the abundance, and that is the relative abundance of the special materials used in the formation of the element in question.

The abundance of the elements in the earth's crust might seem to give the best information in this respect if it were not known that the surface of the earth has been subjected to very long-continued differentiative processes, and so has a very local character. The meteorites, on the other hand, come from much more varied positions in space, and at the same time show much less indication of differentiation. In the meteorites, the elements of even atomic number are on the average about seventy times more abundant than the odd-numbered elements, and, moreover, if the elements are plotted in order of their atomic numbers, it is found that the even-numbered elements are in every case very much more abundant than the adjacent odd-numbered elements. Almost more striking than this is the fact that the first seven elements in the order of their abundance are all even numbered, and, furthermore, make up 98·78% of the material. Both the iron and stone meteorites separately show just these same relations, whether the percentages are calculated as atomic or by weight. Thus the stone meteorites contain 97·6% and the iron meteorites 99·2% of even-numbered elements. It is remarkable, too, that the highest percentage found for any odd-numbered element in any class of meteorites is 1·53%, whilst among the even-numbered elements larger percentages are common, and range up to 90·6%. In the lithosphere, whilst the relationship is not so striking, the even-numbered elements are still seven to ten times as abundant as those which are odd, depending on whether the calculations are made by weight or by atomic percentage. Among the rare earths, the even-numbered elements are the more abundant. Among the radioactive elements, the odd-numbered element is in each case either of a shorter period than the even-numbered, or else is as yet undiscovered. Five elements are as yet unknown, and these are all odd-numbered. The elements of low atomic number are found to be very much more abundant than those of higher atomic number, both in the meteorites and on the earth. Thus the first twenty-nine elements make up about 99·9% of the material, whilst the remaining sixty-three are either extremely rare or comparatively rare. Of the first twenty-nine elements, those with atomic numbers between 6 and 28 include nearly all the material. The above-mentioned results seem to show that the elements fall into two series, as predicted from the helium–hydrogen structure previously described (*loc. cit.*). The variation in the abundance of the elements as found would seem to be the result of an inorganic evolution, which is entirely independent of the Mendeléev periodic system. The formation of the elements seems to be, however, related to the atomic number. The influence of segregation on the composition of the lithosphere is discussed, as well as the effect of the stability of the atoms on their formation. The hydrogen–helium structure of the atoms would therefore seem to be a theory based on evidences as firm as a large number of the generally accepted theories of chemistry and physics, since predictions made in connexion with it have been so strikingly verified. This theory establishes to some extent a normal average composition for material, and in consequence it should have an important bearing on the history of the differentiative processes which have taken place on the earth, and its applications to geology should be far-reaching. J. F. S.

Chinese Alchemy. H. J. Holgen (*Chem. Weekblad*, 1917, **14**, 400—406).—A historical account of alchemy as practised in China, mainly with the object of discovering an "Elixir of Life." A. J. W.

[New Type of Condenser.] H. P. Fishburn (*J. Amer. Chem. Soc.*, 1917, **39**, 1074).—A piece of apparatus is described which will serve as a simple condenser when long-necked flasks are used for reflux work. The condenser consists of a thin-walled glass tube about 0·3 cm. less in diameter than the neck of the flask with which it is to be used. This tube is slightly enlarged at the top and tapered toward the bottom, so that when placed in the neck of the flask it is supported by the enlargement and leaves a space of 0·15 cm. in between the two surfaces. Into the top of the tube a narrow glass tube, which reaches to the bottom of the wider tube, is fused, and an outlet tube is sealed by the side of this at the top. When water circulates through the apparatus, a fairly efficient condenser is produced. J. F. S.

A Convenient Form of Autoclave. George W. Morey (*J. Washington Acad. Sci.*, 1917, **7**, 205—208).—The bomb of the autoclave is made from a piece of 8·7 cm. pipe, the lower end of which is closed by welding on an iron bottom. The upper end is closed by the cover, the outer rim of which presses against an inner shoulder on the outer shell, which is made from 10 cm. pipe. Closure is effected by compression of a gold wire washer, pressure being applied by a bolt threaded through a cross-bar fixed to the lower end of the outer shell.

The autoclave has given highly satisfactory results in experiments with aqueous solutions up to 300°. It is said to be superior to other forms of autoclave in ease of construction, in manipulation, and in certainty of closure. H. M. D.

Inorganic Chemistry.

Action of Sulphur Dioxide on Metal Oxides. I. DALZIEL LLEWELLYN HAMMICK (T., 1917, **111**, 379—389).—The results obtained on heating various metallic oxides in a current of sulphur dioxide show that cupric oxide, bismuth oxide, mercuric oxide, manganese dioxide, and lead peroxide may be grouped together in that the sulphur dioxide undergoes oxidation in contact with each of these. Although the sulphate of the metal is one of the products of the reaction in each case, the actual change varies with the nature of the metal.

The other oxides examined (stannous oxide, lead monoxide, ferrous oxide, and manganous oxide) behave similarly to the alkaline earth oxides in that sulphites appear to be formed as the primary product, which is subsequently transformed into a mixture of sulphides and sulphates. No indication of the actual formation of sulphites has been obtained, but, whatever the first step in the complete reaction may be, the nature of the ultimate products indicates that these oxides have a reducing effect on the sulphur dioxide. H. M. D.

Experiments with Nitrogen Trichloride. C. T. DOWELL and WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1917, **39**, 896—905). —The authors have investigated the action of a solution of nitrogen trichloride in carbon tetrachloride on a number of reducing agents. The nitrogen trichloride was prepared by the action of ammonium chloride on hypochlorous acid in the presence of carbon tetrachloride. The carbon tetrachloride solution, of about 0·1*M* concentration, was preserved in blackened bottles, in which, after some weeks, it slowly decomposed. Of all the reducing agents examined, only one, sodium sulphite, converted the whole of the nitrogen into ammonia; this occurs according to the equation $3Na_2SO_3 + NCl_3 + 3H_2O = 3Na_2SO_4 + 2HCl + NH_4Cl$. In all other cases free nitrogen was also liberated. In the case of arsenious acid (0·123*N*), 7·7% of the nitrogen is liberated, whilst on reducing the concentration by one-half, the amount of nitrogen liberated is increased fourfold. The addition of sulphuric acid increases the amount of nitrogen set free, and this amount increases up to 0·5*N*-sulphuric acid, after which increased concentrations of sulphuric acid have no further action. Hydrogen sulphide sets free about 5·5% of the nitrogen in the elementary condition, the residue being reduced to ammonia. Potassium iodide liberated 18% of the nitrogen as gas. and the addition of sulphuric acid did not change this amount. The reactions with ferrous sulphate were examined, and here also nitrogen and ammonia were formed. Iodine reacts with nitrogen trichloride, setting free nitrogen and forming chlorides of iodine; on the addition of water to the resulting solution, iodic acid is precipitated.

Sodium hydroxide reacts with nitrogen trichloride, giving a rapid evolution of nitrogen, although about 7% of the nitrogen present is recovered as ammonia. Quinol is converted into hexachloroquinol, whilst carbamide in acid solution is not acted on, but in neutral solution there is a slow evolution of nitrogen. Nitrogen trichloride reacts slowly with dilute ammonium chloride solution and more rapidly with a concentrated solution to give nitrogen and hydrogen chloride, $NH_4Cl + NCl_3 = N_2 + 4HCl$. J. F. S.

Reactions between Chlorine and Ammonia. WILLIAM C. BRAY and C. T. DOWELL (*J. Amer. Chem. Soc.*, 1917, **39**, 905—913).—The authors tabulate the reactions which occur when ammonia and chlorine react (*a*) in acid solution, (*b*) in alkaline solution, and (*c*) in dilute solutions of ammonia and hypochlorous acid. Noyes and Lyon (A., 1901, ii, 601) have shown that when chlorine gas reacts with 0·5% ammonia solution, the reaction $3NH_3 + 6Cl_2 = N_2 + NCl_3 + 9H^+ + 9Cl^-$ takes place, in which equimolecular quantities of nitrogen and nitrogen trichloride are produced. This reaction, if it follows the equation, would be of the ninth order, and to ascertain whether this is so, a number of experiments have been carried out on the reaction between gaseous chlorine and ammonium hydroxide. From the results of these experiments, it is concluded that the above equation is only the resultant of a number of intermediate reactions, the first of which is the formation of monochloroamide, NH_2Cl, according to the equation $NH_3 + Cl_2 = HCl + NH_2Cl$. J. F. S.

Some Compounds of Boron, Oxygen, and Hydrogen. MORRIS W. TRAVERS, N. M. GUPTA, and R. C. RAY (Pamphlet, 1916, pp. 46. Compare A., 1912, ii, 938).—Further investigation of the reaction between magnesium boride and water, and of the nature of the substances present in the resulting solution, has shown that many of the conclusions drawn from the previous observations (*loc. cit.*) require correction.

The new experiments show that when a mixture of 2¼ parts of magnesium powder and 1 part of anhydrous boric acid is heated in a current of hydrogen until the reaction is complete, solutions are obtained by treatment of the product with water which are free from boric acid and magnesium borate, and contain only substances which are described as borohydrates. The main product of the action of water is an insoluble compound of magnesium oxide with a borohydrate, reaction taking place in accordance with the equation $Mg_3B_2 + 6H_2O = Mg_3B_2(OH)_6 + 3H_2$. The soluble borohydrates and gaseous compounds of boron and hydrogen, which are also formed, are attributed to secondary reactions.

The solutions of the borohydrates are unstable, but the stability is increased in presence of traces of ammonia. On the addition of acids to the solutions, hydrogen is evolved, and the acid solutions decolorise iodine. Analyses and molecular weight determinations indicate that the mean composition of the borohydrates is represented by $H_6B_2O_2$. When the solutions are evaporated to dryness and the residue heated, a mixture of the oxide, B_2O_2, with magnesium oxide is obtained.

If the mixture of magnesium boride and boric acid is insufficiently heated, or if excess of boric acid is employed in preparing the mixture, the solutions obtained by the action of water differ from those described above in that they contain magnesium borate and boric acid, as well as one or more borohydrates.

When magnesium boride, after prolonged treatment with water, is acted on by strong ammonia, a solution is obtained which does not lose hydrogen when kept in an exhausted tube, and does not oxidise in contact with the air. On addition of acids to this solution, hydrogen is rapidly evolved, and the acid solution reacts with iodine. When the solution is evaporated to dryness at low temperature in a vacuum, a white, crystalline residue remains which gives off hydrogen when heated, and is transformed into the oxide, B_4O_5. This oxide dissolves in water with the formation of a yellow solution, which rapidly absorbs oxygen in contact with the air, the reaction being represented by the equation $2B_4O_5 + O_2 + 12H_2O = 8B(OH)_3$.

Molecular weight determinations of the substance in the ammoniacal solution prepared as described above seem to show that the compound has the formula $H_{12}B_4O_6,2NH_3$. When ammoniacal solutions of the borohydrates are evaporated to dryness and treated with water, a small quantity of insoluble residue is left which appears to be a hydrated derivative of an oxide containing less oxygen than those previously referred to.

The constitution of the borohydrates is discussed on the basis of the chemical and physical properties of the solutions.

H. M. D.

Preparation of Carbon Suboxide from Malonic Acid and Phosphoric Oxide. Alfred Stock and Hugo Stoltzenberg (*Ber.*, 1917, **50**, 498—502).—The poor yields of carbon suboxide which are usually obtained by the action of phosphoric oxide on malonic acid are largely due to the polymerisation of the suboxide under the catalytic influence of the dehydrating agent. If the suboxide is removed rapidly by carrying out the reaction in a good vacuum and condensing the product by means of liquid air, a volume of the gas corresponding with as much as 25% of the malonic acid can be obtained. An apparatus is figured and its manipulation described whereby the whole process, inclusive of the removal of the acetic acid formed, by means of a lime tower, and the fractional distillation of the carbon dioxide and suboxide mixture can be carried out in a comparatively short time.

Carbon suboxide has m. p. −111·3°, vapour pressure at 0°, 587—589 mm., and b. p. 6°. The polymerisation of the gas to the red substance, which is soluble in water, is catalysed remarkably by the polymeride itself. The gas may sometimes be kept for days, but as soon as polymerisation sets in, it completely disappears within a day. In contact with phosphoric oxide, the gas polymerises in a fraction of a minute. Carbon suboxide is very soluble in carbon disulphide or xylene. It is completely converted into malonic acid by means of water, so a few drops of water serve as an excellent gasometric absorbent for the gas.

J. C. W.

A Simple Method of Preparing Potassium Stannichloride. John Gerald Frederick Druce (T., 1917, **111**, 418—419).—A concentrated solution containing potassium chloride and stannous chloride in the molecular ratio 2:1 is acidified with hydrochloric acid and subjected to the action of chlorine. The resulting solution yields crystals of potassium stannichloride when slowly evaporated at 50—70°. H. M. D.

New Acid Sodium Phosphate and its Action on Glass, Porcelain, Silica, Platinum, and Nickel Vessels. John H. Smith (*J. Soc. Chem. Ind.*, 1917, **36**, 419—420).—The salt is easily prepared in an impure condition by evaporating mixtures of sodium hydroxide or sodium carbonate with a sufficient proportion of phosphoric acid and igniting the residue. It forms a fused, glassy mass which dissolves slowly in cold, but more readily in warm water, and is nearly neutral to methyl-orange or phenolphthalein. The name *sodium polyphosphate* is proposed. Its powerful corrosive action renders it almost impossible to obtain the substance in a pure condition or to determine its exact composition, which, however, is probably expressed by the formula $Na_4P_6O_{17}$.

A remarkable property of sodium polyphosphate is its exceedingly energetic action on glass, porcelain, platinum, and silica vessels. The action is naturally most powerful at the high temperature of fusion, the glaze of porcelain dishes being eaten into and leaving, after solution of the salt, a deposit of granular silica. Silica vessels were also sensibly attacked, and silica entered into the composition of the resulting salt. A platinum dish was strongly attacked and became brittle wherever it had been in contact with the fused salt. A nickel vessel was corroded until the residue consisted entirely of nickel and sodium pyrophosphates. H. W.

Constitution of the Alkali Phosphates and some New Double Phosphates. John H. Smith (*J. Soc. Chem. Ind.*, 1917, **36**, 420—424).—When attempts are made to prepare disodium hydrogen phosphate by the treatment of phosphoric acid with the calculated quantity of sodium hydroxide or carbonate, the resulting solution can only be caused to crystallise with considerable difficulty. The salt which separates has the composition

$$17Na_2HPO_4,Na_3PO_4,$$

whilst the mother liquor contains the excess of phosphoric acid in the form NaH_2PO_4. The following double phosphates are also described, in which, however, the water of crystallisation, although always very considerable, has not been determined:

$$8Na_2HPO_4,Na_3PO_4,$$

thin laminæ belonging apparently to the mono- or tri-clinic systems;

$6Na_2HPO_4,Na_3PO_4$, fine, rhombic tables with angles of 66°; $3Na_2HPO_4,Na_3PO_4$, rhombic pyramids with basal planes in parallel grouping forming radiating spires; $3Na_2HPO_4,2Na_3PO_4$, fine needles.

Sodium dihydrogen phosphate crystallises as such from its aqueous solution.

Sodium polyphosphate (compare preceding abstract) could not be crystallised from water, since, on prolonged boiling, it is transformed into orthophosphoric acid and sodium metaphosphate.

Attempts are also recorded to obtain trisodium phosphate by crystallisation from solutions of equivalent quantities of phosphoric acid and sodium hydroxide; the crop so obtained had the approximate composition $2Na_3PO_4,Na_2HPO_4$, whilst the mother liquor gave feathery crystals of the composition $18Na_3PO_4,Na_2O$. A similarly constituted salt was obtained by direct crystallisation when a 4% excess of sodium hydroxide was used.

In the manufacture of trisodium phosphate, the best method appears to consist in the use of sodium carbonate for the first stage and sodium hydroxide for the second stage, employing the proportions indicated by the equations: $36H_3PO_4 + 37Na_2CO_3 = 34Na_2HPO_4 + 2Na_3PO_4 + 37CO_2 + 37H_2O$ and

$$34Na_2HPO_4 + 2Na_3PO_4 + 38NaOH = 36Na_3PO_4 + 2Na_2O + 36H_2O$$

H. W.

Ammonium Thiosulphate-Polythionate Solutions. A Contribution to Liquid Purification of Coal Gas. E. V. ESPENHAHN (*J. Soc. Chem. Ind.*, 1917, **36**, 483—489).—The actions occurring between ammonium thiosulphate, ammonium polythionate, sulphur dioxide, and ammonia have assumed practical importance since the introduction of the Feld method of utilising the sulphur contained in the coal for the fixation of ammonia without first forming sulphuric acid (compare A., 1912, ii, 448). The following are the chief results of an investigation of the interaction of these substances.

The reaction between thiosulphate and sulphur dioxide is expressed by the equation: $2(NH_4)_2S_2O_3 + 3SO_2 = (NH_4)_2S_3O_6 + (NH_4)_2S_4O_6$. Under certain conditions, other reactions occur according to the equations (1) $2(NH_4)_2S_2O_3 + 3SO_2 + S = 2(NH_4)_2S_4O_6$, and (2) $2(NH_4)_2S_4O_6 = (NH_4)_2S_3O_6 + (NH_4)_2S_5O_6$; these, however, do not influence the main reaction.

Although the reaction between polythionate and ammonia solution as expressed by the products of the reaction appears uniform, it actually proceeds between two extremes represented by the equations: $3(NH_4)_2O,OH_2 + 2(NH_4)_2S_nO_6 = 5(NH_4)_2S_2O_3 + 3H_2O$ (where $n = 5$), and $(NH_4)_2O,OH_2 + (NH_4)_2S_nO_6 = (NH_4)_2S_2O_3 + (NH_4)_2SO_4 + H_2O$ (where $n = 3$).

The reactions between tri-, tetra-, and penta-thionate and potassium or sodium hydroxide may take place separately according to equations: $10KOH + 2(NH_4)_2S_5O_6 = 5K_2S_2O_3 + 4NH_3 + 7H_2O$; $6KOH + 2K_2S_4O_6 = 3K_2S_2O_3 + 2K_2SO_3 + 3H_2O$; and

$$6NaOH + 2Na_2S_3O_6 = Na_2S_2O_3 + 4Na_2SO_3 + 3H_2O.$$

The velocities of the five above-mentioned reactions greatly increase with rise of temperature.

Sulphur dioxide is not absorbed by ammonium thiosulphate in the presence of ammonia unless polythionate is present in the solution. It is then added to form polythionate, which does not decompose to sulphate at 100°, so that the amount of sulphate formed for each ammonium concentration is the same as with polythionate and ammonia.

When ammonia acts on ammonium polythionate and sulphur dioxide in the presence of hydrogen sulphide (that is, ammonia and ammonium sulphide), less sulphate is formed than in the absence of hydrogen sulphide and the velocity of the reaction is considerably greater.

Certain modifications of the Feld process for ammonia recovery are suggested. H. W.

Solubility of Calcium Sulphite in Water and Sugar Solutions. T. VAN DER LINDEN (*Mededeel. Proefstat. Java Suckerindustrie*, 1916, **6**, 307—322; from *Chem. Zentr.*, 1917, i, 366).—The experiments were performed by titrating 100—200 grams of solution with *N*/100-iodine. The results show that the solubility of calcium sulphite in water and sugar solutions is very slight. In the latter case the solubility is greater than in the former and is greatly depressed by the presence of gypsum. The solubility of calcium sulphite diminishes with rising temperature.

H. W.

Effect of Adsorption on the Physical Character of Precipitated Barium Sulphate. HARRY B. WEISER (*J. Physical Chem.*, 1917, **21**, 314—333).—The conditions which affect the form in which barium sulphate is precipitated are discussed by the author, and a series of experiments is described which indicates the effect, on the nature of the precipitate, when barium sulphate is formed under different conditions. It is shown that barium sulphate has a marked tendency to adsorb many other substances. Since any substance which is adsorbed by a second will tend to peptise the latter, it follows that, other conditions being the same, barium sulphate will be deposited in the most finely divided state when precipitated in the presence of those substances for which it has the greatest specific adsorption. In accordance with the general rule, barium sulphate shows a marked adsorption for its own ions. Positive colloidal solutions of barium sulphate, stabilised by preferential adsorption of barium ion, have been prepared by Kato and Recoura (A., 1910, ii, 850; 1908, ii, 692); the present author has now prepared a negative colloidal solution of barium sulphate, stabilised by preferential adsorption of sulphate ions. This was done by adding 0·1*N*-sodium sulphate in slight excess to a 0·1*N*-solution of barium chloride in a 1:5 glycerol–water solution. Barium sulphate is deposited in a much finer state when precipitated with barium chloride in excess than with sulphuric acid in excess. Finer crystals are also obtained from potassium sulphate solutions. This is explained as follows. Barium sulphate adsorbs its own ions strongly and hydrogen ions are much more strongly adsorbed than other cations. When sulphuric acid is precipitated by barium chloride, the precipitate tends to deposit in a finely divided state because of the relatively strong adsorption of barium ions and hydrogen ions. It would also be deposited very finely divided from sulphuric acid solution were it not that the strongly adsorbed hydrogen ion diminishes the adsorption of the sulphate ion. From potassium sulphate solution it is precipitated finely divided, since the potassium ion is not strongly adsorbed. In the presence of hydrochloric acid, barium sulphate is deposited more finely divided with the barium ion in excess than with the sulphate ion in excess. In the first case, the cations hydrogen and barium are strongly adsorbed; in the second case, the presence of the sulphate ion diminishes the adsorption of the hydrogen ion. Barium sulphate is always more coarsely crystalline when precipitated in the presence of an appreciable amount of hydrochloric acid. This is due to the solvent action of hydrochloric acid. In the presence of considerable excess of hydrochloric acid the solvent action of the hydrochloric acid is the predominant factor. J. F. S.

Physico-chemical Foundations of the Commercial Zinc Extraction. M. BODENSTEIN and SCHUBART (*Zeitsch. Elektrochem*, 1917, **23**, 105—116).—The temperature at which the system zinc oxide and carbon under four different pressures (28 mm., 87 mm., 266 mm., and 760 mm.) is converted into zinc vapour and carbon monoxide has been measured. Three different methods were employed: (1) thermal analysis, (2) observation of the point at which the mixed materials lost weight, and (3) measurement of the velocity of the evolved gases. In all cases approximately the same temperature was obtained, 1033°, which is the same as that previously obtained by Johnson (*Electrochemical Industry*, 1904, 185). These values were regarded as equilibrium values and used to calculate the heat of the reaction, whereby impossible values were obtained. Consequently, the observed temperatures represent points at which the reaction is sufficiently rapid to be observed. The true equilibrium was obtained in a quartz apparatus; this set in extremely slowly, but a pressure of 1 atmosphere was obtained at 780°. An exact calculation of the experimental results has not been possible, since for this a knowledge of the vapour pressure of zinc and of the equilibrium between carbon, carbon monoxide, and carbon dioxide is necessary, and these are not known with sufficient accuracy. The possibility of extracting zinc by the use of high pressures or catalysts in a reducing atmosphere is discussed.

J. F. S.

Zinc Chromates and their Significance for the Colour Industry. LAURENZ BOCK (*Kolloid Zeitsch.*, 1917, **20**, 145—150).—A discussion of the various basic zinc chromates and alkali zinc chromates which have been described in the literature with reference to the use of zinc yellow in the pigment industry. H. M. D.

Zinc Platinichloride. AUGUST EBERHARD (*Arch. Pharm.*, 1917, **255**, 65—72).—In endeavouring to prepare a platinichloride of the reduction product obtained by the action of zinc and dilute sulphuric acid on bromoscopoline, the author obtained red crystals of the composition $ZnPtCl_6,6H_2O$, whereas, according to the earlier descriptions of zinc platinichloride, this salt is yellow. Careful examination showed that the red colour was due to the presence of a little zinc platinibromide as impurity.

In dry air the platinichloride hexahydrate is stable, but in moist air it slowly deliquesces. Contrary to the statement of Topsoë (*Oversigt K. Danske Videnskab. Selsk*, 1868, 151), the hexahydrate does not lose $4H_2O$ at 100—100·5°, but a temperature of 102—103° is necessary; the remaining $2H_2O$ is slowly eliminated above 130°.

D. F. T.

General Method for obtaining Metals in a Metalloidal Condition. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1295—1314).—The author gives the results of the application of the views previously expressed to various regions of physicochemical phenomena (A., 1913, ii, 753; 1915, ii, 411; 1916, ii, 185).

Investigation of the colour of disperse systems with metallic disperse phases and of the colour of the disperse molecules with the aid of the ultramicroscope shows that, as regards their colour, such systems form two groups. The first contains relatively coarsely-disperse systems, and the disperse particles in them still retain metallic reflection and dispersion, and the second the comparatively highly disperse systems with disperse particles exhibiting the optical properties of non-metallic substances, that is, of substances with so-called internal colour. In the first group the colour changes with the degree of disperseness exactly as in coarsely disperse systems of metalloidal selenium, and in the second group as with a transparent, coloured substance which absorbs the red and blue parts of the spectrum and transmits orange, yellow, and green light.

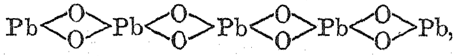
These two groups of disperse systems of one and the same element contain the latter in two different states, namely, the metallic and the metalloid, the optical properties being different in the two cases. No sharp line separates these two states, intermediate stages being quite possible. Such measurements as those of Galli ("Das optische Verhalten dünner Metallschichten," Diss., Göttingen, 1913) on the index of refraction of thin layers of silver deposited on glass by cathodic disintegration show that at a sufficiently high degree of dispersion even typical metals pass from the metallic to the metalloidal condition. The value of the refractive index of the transparent, intensely coloured metalloidal substance then obeys the same rule as for all metalloids.

Of the three known modifications of selenium, the author has investigated two: (1) the red, crystalline metalloidal form which melts at 170—180° when rapidly heated and at 150° is converted into the metallic modification melting at 217°. The latter form is not transformed on cooling into the red variety, which is obtainable only by quickly cooling the fused metallic selenium from a temperature of 250°. Thus, in the coarsely disperse condition, on rise of temperature, red metalloidal selenium ⟶ grey metallic selenium. If, however, the condition is sufficiently highly disperse, the reverse change may be induced. Further, Saunders found that grey metallic selenium, when finely powdered, is converted into the red metalloidal form, which at about 200° is transformed into the grey variety, and so on.

The conditions which give rise to the metallic and metalloidal states are discussed and also the regions over which they are capable of existing. T. H. P.

Arsenates of Lead. III. Basic Arsenates. C. C. McDonnell and C. M. Smith (*J. Amer. Chem. Soc.*, 1917, **39**, 937—943. Compare A., 1916, ii, 620; this vol., ii, 33).—The basic lead arsenate, $8PbO,As_2O_5,\frac{1}{2}H_2O$, was first prepared by Strömholm (A., 1904, ii, 258); the authors have confirmed the formation of this compound, and have shown that it may be obtained by dissolving dilead arsenate in a 10% solution of sodium hydroxide to saturation, filtering, and pouring the solution into about five times its volume of boiling water. On cooling, very thin, square plates separate, which are biaxial and positive. They have D_{15}^{15} 8·04, and may be fused without change except for the loss of water. The authors term this substance octa-lead arsenate. The basic lead arsenate, $Pb_4(Pb{\cdot}OH)(AsO_4)_3,H_2O$, prepared by the action of ammonia on dilead arsenate, has been obtained crystallised in hexagonal prisms terminated by the basal pinacoid, frequently with the corners truncated by the second order pyramid. They have parallel extinction and are uniaxial with low negative birefringence; the average index of refraction is about 2·09. D 6·86. These crystals are similar to the crystals of mimetite; consequently, the authors have termed this substance *hydroxymimetite*. A new basic lead arsenate, $Pb_5[Pb(OH)]_2(AsO_4)_4$, is obtained by saturating 10% potassium hydroxide with dilead arsenate and pouring the solution into twenty times its volume of boiling water. On cooling, small, prismatic crystals separate which have D_{15}^{15} 7·08; they are doubly refractive, with parallel extinction, negative elongation, and index of refraction 2·07. J. F. S.

Polysilicates and Polyplumbates. Georg Kassner (*Arch. Pharm.*, 1917, **255**, 130—134).—In a commentary on Pükall's paper on the hydrothermal decomposition of polysilicates (A., 1916, ii, 322), the author directs attention to his work on polyplumbates (A., 1895, ii, 14; 1896, ii, 247), in which calcium di- and tetraplumbates were described. The more recent discovery of lead triplumbate,



$Pb<^{O}_{O}>Pb<^{O}_{O}>Pb<^{O}_{O}>Pb<^{O}_{O}>Pb$,

by Fischer and Ploetze (A., 1912, ii, 555) serves to bring lead still further into line with silicon in the production of poly-acids. In the case of tin, the compound $H_2Sn_5O_{11}$ is the only representative known as yet.

There is one outstanding difference between polyplumbates and polysilicates, however. Whereas the former are produced by the hydrothermal treatment of ortho-plumbates, the latter suffer decomposition when heated with small quantities of water under pressure. J. C. W.

Influence of Arsenic in Brass. Oliver Smalley (*J. Soc. Chem. Ind.*, 1917, **36**, 429—439).—The author has carried out an extensive investigation on the influence of arsenic in brass, and draws the following conclusions. Arsenic renders brittle all copper–zinc alloys, commercially known as 'brass,' when it is present as free arsenide; this compound is a weak, brittle constituent, and, if present in sufficient quantity, completely envelops each crystal grain, thus producing a crystalline mass the grains of which are stronger than the junctions. It therefore acts in the same manner as antimony, bismuth, and other metals which form definite intermetallic compounds the presence of which produces 'intercrystallinity.'

The films of arsenide do not affect the cold-working properties of α-brasses to any appreciable extent owing to the ready accommodation of this class of brasses to plastic deformation without rupture.

Small quantities of arsenic (under 0·10%) are beneficial to α-brasses, no matter what their physical condition; this is due to the arsenic entering mainly into solid solution, the amount remaining as free arsenide being negligible when considered as a mechanical enclosure.

A complete recovery of the ductility of all essentially cold-working arsenical brasses containing under 0·5% arsenic is effected by cold-working and subsequent annealing, this treatment causing a complete solution of arsenide which is beneficial to the quality of the brass when present in quantities not exceeding 0·20%; between 0·2% and 0·5% the brass possesses the same properties as a non-arsenical brass. When the arsenic present exceeds 0·5%, the brass becomes intercrystalline whatever the physical condition of the arsenide may be. It thus appears that the physical properties of arsenical α-brasses containing less than 0·5% As are governed by the physical condition of the brass; when exceeding that amount, the percentage of arsenic governs the physical properties, no matter what be the physical condition of the alloy.

The temperature at which α-phase brasses containing free arsenide will anneal is 30—50° higher than that of pure non-arsenical brass; data are not yet available concerning the influence of arsenic on recrystallisation when present in perfect solid solution in the copper–zinc as a perfectly homogeneous alloy.

Arsenic when present even in the most minute quantities is detrimental to the physical properties of hot-worked brass, although it in no way affects the hot-working properties.

Arsenic does not assist in any structural inversion of the β-constituent when cooled under normal conditions. H. W.

Composition of a Bronze Age Wind Instrument. F. Rathgen (*Zeitsch. anal. Chem.*, 1917, **56**, 144—148).—The tubular portion of the instrument examined consisted of: copper, 85·03%; tin, 13·76%; lead, 0·10%; iron, 0·37%; cobalt, 0·54%; arsenic and sulphur, traces. Other portions of the instrument had similar, but slightly different, compositions. W. P. S.

An Improved Mercury Still. L. H. Duschak and S. O. Spencer (*J. Physical Chem.*, 1917, **21**, 311—313).—A modification of the Weinhold mercury distillation apparatus is described; it consists of the ordinary vacuum distillation apparatus, to which a device is added whereby a small quantity of air is allowed to bubble into the distillation bulb at a definite rate. By this means the distillation takes place in a partial vacuum and not in a Torricellian vacuum as hitherto. The advantage claimed for the modified apparatus is that those metals which generally accompany mercury are oxidised during the distillation and are thereby more effectively separated than by ordinary distillation. J. F. S.

Some Rare Earth Compounds. A. J. Grant and C. James (*J. Amer. Chem. Soc.*, 1917, **39**, 933—937).—With the object of finding methods for rapidly separating the rare earth compounds, the authors have determined the solubility of a number of oxalates in 20% solutions of methylamine oxalate, ethylamine oxalate, and triethylamine oxalate. The following amounts of rare earth oxalate, expressed in grams of M_2O_3, dissolve in 100 c.c. of the solution: (i) Methylamine oxalate, neodymium, 0·027; gadolinium, 0·069; dysprosium, 0·276; yttrium, 0·877; thulium, 4·082; and ytterbium, 5·242. (ii) Ethylamine oxalate, neodymium, 0·107; gadolinium, 0·360; dysprosium, 1·787; yttrium, 1·653; thulium, 5·728; and ytterbium, 5·858. (iii) Triethylamine oxalate, lanthanum, 0·032; neodymium, 0·065; gadolinium, 0·883; dysprosium, 1·432; yttrium, 1·006; thulium, 1·340; and ytterbium, 2·048. These figures indicate that there is no great variation in the series of the solubilities. Several new salts are described. *Neodymium diphenylsulphonate*, $(C_6H_5\cdot C_6H_4\cdot SO_2\cdot O)_3Nd,6H_2O$, is prepared by adding an acidified solution of the sodium salt to a solution of neodymium chloride; the salt is sparingly soluble in water and separates as a mass of light pink crystals. *Neodymium ferricyanide*, $NdFe(CN)_6,4H_2O$, is formed when a mixture of concentrated solutions of potassium ferricyanide and neodymium chloride is boiled. The salt separates as a brick-red powder which has an orange tint and is very slightly soluble in water. *Lanthanum ferricyanide*, $LaFe(CN)_6,4H_2O$, is prepared in the same way as the neodymium salt; it is slightly more soluble and does not possess such a rich colour. *Yttrium ferricyanide*, $YFe(CN)_6$, is precipitated from a mixture of dilute solutions of potassium ferricyanide and yttrium chloride. The ferricyanides of erbium, thulium, and ytterbium are less soluble than the yttrium salt; hence the precipitation of the ferricyanide would appear to be a possible method for the separation of the yttrium earths. This was proved in the following case: an impure yttrium preparation containing erbium and of mean atomic weight 104·90 was dissolved in hydrochloric acid, the solution just neutralised, and boiled. To the boiling solution potassium ferricyanide was added. The precipitate was treated with sodium hydroxide, filtered, washed, dissolved in hydrochloric acid, and precipitated with oxalic acid. The oxalate was ignited, and the process repeated with the filtrate and a second fraction obtained. The fifth fraction had a mean atomic weight of 93·00. The authors emphasise the fact that the yttrium earth ferricyanides are considerably less soluble than has hitherto been believed, and express the opinion that the above method of separation is the most rapid known.

In connexion with the preparation of neodymium diphenylsulphonate, the authors experienced difficulty in the preparation of diphenyl by the method of passing benzene vapour through a hot tube, and have devised a method of preparing this substance which rapidly gives a good yield of the hydrocarbon. A quantity of benzene is placed in a wide-necked flask, fitted with a condenser, in which above the benzene layer a length of nichrome ribbon is suspended. The ribbon is connected with an alternating circuit. The benzene is boiled for a few minutes by means of a flame, and then current is allowed to flow through the ribbon so that it is raised to dull redness. The flame is then extinguished and the benzene kept boiling for five to seven hours by the heat from the wire. At the end of this period the liquid in the flask will solidify when cooled. J. F. S.

The Action of Acetic Acid on Aluminium. RICHARD SELIGMAN and P. WILLIAMS (*J. Soc. Chem. Ind.*, 1917, **36**, 409—415. Compare A., 1916, ii, 187).—In continuation of their previous experiments, the authors have investigated the action of boiling dilute acetic acid, and also of acetic acid of all concentrations at the ordinary temperature, on aluminium. In addition, the effect of the presence of small quantities of various substances in the acetic acid has been determined.

The aluminium, containing Al=99·1%, Si=0·45%, Fe=0·45%, Cu=0·00%, was used in the form of thin, rolled strips which were generally annealed at 450° for three hours before use. The surface was cleaned with sodium hydroxide and washed with dilute nitric acid previous to determining the rate of dissolution.

As in the case of the more concentrated acids, the rate of dissolution of aluminium in boiling dilute acetic acid is found to rise continuously until the concentration of the acid falls to 1%. With more dilute acid, it is impossible to obtain trustworthy data as the metal becomes coated with a protective skin. The rate of dissolution is greatly affected by the products of the interaction, the disturbance growing very rapidly with increasing dilution. A definite reason cannot yet be assigned, but it has been shown that acid which has become highly active towards aluminium can be distilled without change in its activity.

Solutions of acetic acid boiled in contact with aluminium become turbid after a period which is short or long according to the concentration of the acid; the nature of the turbid solutions varies in the different cases. With acids of concentration between 60% and 5% the turbidity disappears on keeping or on addition of dilute hydrochloric acid. Little or no deposit is formed on the aluminium strip, and if any deposit is formed it is always loosely attached and readily removable. Such turbidity appears to be due to the separation of basic acetate or acetates of aluminium. In the case of acids of about 0·2% concentration, the turbid solutions do not become clear on keeping, and the addition of dilute hydrochloric acid or sodium hydroxide produces a flocculent precipitate which does not readily dissolve in boiling dilute hydrochloric acid. Such solutions give rise to a deposit which adheres firmly to the aluminium and is not readily removed either by chemical or mechanical means. It is considered that in these cases the turbidity may be due to the formation of a colloidal solution of aluminium hydroxide. Solutions containing between 5% and 0·2% of acetic acid yield turbid solutions of an intermediate character.

Except in the case of the anhydrous acid, aluminium is uniformly attacked by boiling acetic acid at all concentrations; no evidence of local action has been observed.

In general, aluminium is only slowly attacked by cold acetic acid; the rate of dissolution increases with increasing dilution of the acid, the highest rate so far observed occurring with an acid containing 0·02% acetic acid. The rate is frequently high at first, but rapidly falls, and then remains constant over long periods. In most cases the attack is uniform, but local action has been observed at concentrations between 70% and 95%, and in cases in which the metal has been allowed to remain in contact with thin films of dilute acid which have thereby become subjected to extensive aeration. The main factor in determining local action appears to be the presence of oxygen, although there is evidence that some other factor also plays a part.

The action of boiling acetic acid (about 10%) on aluminium is practically unaffected by the addition of up to 1% of sodium chloride, potassium bromide, iodide, or nitrate, whereas an equivalent amount of sodium sulphate raises the rate of dissolution appreciably. With the cold acid, on the other hand, the rate of dissolution is increased tenfold by 1% of sodium chloride, whereas potassium bromide effects a smaller increase and potassium iodide and nitrate are without action; 0·5% of sodium sulphate causes a fourfold increase in the rate of dissolution. With cold concentrated acid (about 80%) a marked increase is produced by 1% of sodium chloride, a smaller increase by potassium bromide or iodide, no effect by sodium sulphate, and a decrease by potassium nitrate. The most serious effect of the addition of substances was noted in the case of the boiling, 80% acid. Here the rate of dissolution is raised by 1% of sodium chloride from 290 to 16,000; by 1% of potassium bromide the rate is only increased from 290 to

485, whilst potassium iodide and potassium nitrate are practically without effect. Sulphuric acid (0·5%) in the form of sodium sulphate somewhat increases the rate of dissolution.

The enhanced effect of chlorides as compared with bromides is shown to be due to the fact that aluminium is more readily attacked by hydrochloric than by hydrobromic acid. The influence of iodides in cold solution is due to the separation of free iodine; if the latter is removed the rate of attack falls to that of the acid alone.

In cases in which the acid alone attacks aluminium uniformly, a uniform attack was also observed in the presence of the salts investigated; where, however, the acids alone caused local action, such action was generally promoted by the presence of halogens, retarded by small quantities of sulphuric acid, and absolutely inhibited by as little as 0·1% of nitric acid. H. W.

The Refractory Properties of Clay. H. LE CHATELIER and F. BOGITCH (*Compt. rend.*, 1917, **164**, 761—767. Compare Mellor and Moore, *Trans. English Ceramic Soc.*, 1916, **15**, 77).—An examination of the behaviour of clays of varying composition when submitted to varying pressures at high temperatures. Up to 1100° the resistance to pressure remains invariable. At higher temperatures the material yields increasingly and becomes plastic, the resistance falling rapidly above 1200°. The effect of varying the three factors, time, pressure, and temperature, has been studied. With pressures of 10 kilos. and 1 kilo./cm.^{2} the differences between the temperatures causing the same yielding of the clay are much less than might be expected, not reaching 50° for this pressure range. Varying the temperature of preliminary heating of the brick from 1200° to 1430° has much the same effect. Increasing the purity of the clay used increases the resistance of the brick to temperature and pressure. W. G.

Constitution of Manganic Compounds. M. SEM (*Zeitsch. Elektrochem.*, 1917, **23**, 98).—Polemical, in which the author defends his position (A., 1915, ii, 777) against the criticism of J. Meyer (A., 1916, ii, 483). J. F. S.

The Nature of Subsidiary Valencies. XIV. Influence of Valency on the Energy of Subsidiary Valencies. FRITZ EPHRAIM and SEB. MILLMANN (*Ber.*, 1917, **50**, 529—541).—It was to be expected from the Abegg-Bodländer theory that the stability of metal ammines would rise with increasing valency of the central metallic atom, and so, in order to demonstrate this, the vapour tensions of ferrous and ferric, chromous and chromic, thallous and thallic, and platinous and platinic hexammines have been measured. The equilibria are particularly difficult to reach in the case of tervalent metals, owing to the formation of solid solutions on decomposition, but the data are in agreement with the expectation, except in the case of iron, in which the ferrous hexammines are the more stable.

Ferric Compounds. [For the ferrous compounds see A., 1913, ii, 496.]—The following *ammines* are mentioned: $Fe_2(SO_4)_3,12NH_3$; $FeBr_3,6NH_3$, a dark brown, granular powder; $FeCl_3,6NH_3$, a very voluminous, pale yellow powder, which is unique in being more stable than the corresponding bromide.

In order to test whether the ferric chloride hexammine just mentioned really has the unusual stability, an attempt was made to prepare it from the double salt, K_2FeCl_5. This absorbs ammonia much more slowly than ferric chloride, and the *hexammine* decomposes at a much lower temperature. It appears, therefore, that the double salt as such forms a hexammine, and not that it is first dissociated to give the ammine of ferric chloride. It is not common to get ammines of double salts, for in most cases dissociation takes place. Thus, the red salt, $KCuCl_3$, gives merely the hexammine of cupric chloride, and double alkali–nickel chlorides give the hexammine of nickel chloride. (These double chlorides are obtained by melting the component chlorides together. The fusion is indigo-blue, but passes through reddish-brown to yellow.)

Aluminium Compounds.—The aluminium haloids absorb at least six molecules of ammonia at the ordinary temperature, and the stability of the ammines varies from one halogen to the other many times more than in any other observed case.

Chromium Compounds.—White chromous chloride forms a violet triammine and an ashy-grey hexammine. The following chromic salts are mentioned: $Cr(NO_3)_3,6NH_3$ explodes on heating quickly; $[Cr(NH_3)_6](NO_3)Br_2$, long, yellow prisms; $Cr_2(SO_4)_3,6NH_3$; the hexammines (?) of the haloids and phosphate give no trustworthy tension data.

Thallium Compounds.—Thallous sulphate and chloride do not react with ammonia; the thallic salts give the *ammines*, $Tl_2(SO_4)_3,10NH_3$, and $[Tl(NH_3)_6]TlCl_6$.

Platinum Compounds.—Platinous chloride gives a tetrammine and a pentammine, and the iodide combines with 2, 4, and 6 molecules of ammonia. J. C. W.

History and Preparation of Cobalt Hygrometers. LUDWIG VANINO (*Arch. Pharm.*, 1917, **255**, 81—85).—Although cobalt salts were used in sympathetic inks as long ago as 1706 (see A., 1916, ii, 135) it was not until about 1870 that they began to be used in toy hygrometers. J. C. W.

Recovery of Molybdic Acid. PAUL RUDNICK and R. D. COOKE (*J. Ind. Eng. Chem.*, 1917, **9**, 109—110).—Molybdic acid may be recovered from titration liquors and filtrates containing excess of ammonium molybdate by adding an excess of ammonium phosphate, the collected yellow precipitates being washed by decantation with hot water and dried on a steam-bath. Five hundred and ten grams of the dried salt, containing about 92% of molybdic acid, are dissolved in ammonium hydroxide, and 85 grams of magnesium nitrate are added. After keeping two to three hours, the clear, supernatant liquid is tested for phosphorus by adding a small quantity to twice its volume of nitric acid, when, in the absence of a yellow precipitate, the magnesium ammonium phosphate is filtered off, the filtrate made up to 2000 c.c., and added slowly, with constant stirring, to 2000 c.c. of concentrated nitric acid diluted to 4668 c.c. with water. After keeping for several days and filtering, a further 320 c.c. of concentrated nitric acid are added and the solution is ready for use. G. F. M.

Recovery of Ammonium Molybdate from the Filtrates obtained in the Estimation of Phosphoric Acid. H. KINDER (*Stahl u. Eisen*, 1916, **36**, 1094; from *Chem. Zentr.*, 1917, i, 530).—The following method is stated to be more simple than that described by Friedrich (A., 1916, ii, 490). The molybdic acid is precipitated by adding sodium phosphate to the solution, and the yellow precipitate is washed, by decantation, with 0·1% sodium sulphate solution until free from soluble phosphate and iron salts. The precipitate is then dried; each 325 grams of it is dissolved in 1100 c.c. of ammonia (D = 0·96), the solution is treated with a mixture of 30 grams of magnesium chloride and 30 grams of ammonium chloride dissolved in water to make 100 c.c.; the precipitate is separated by filtration, and each 420 c.c. of filtrate is mixed with 1200 c.c. of nitric acid (D 1·2). The blue molybdic acid residues obtained in the gravimetric estimation of phosphoric acid may be treated in a similar way (dissolved in ammonia, acidified with nitric acid, precipitated with sodium phosphate, etc.).
W. P. S.

Preparation of Pure Zirconium Oxide Free from Iron. K. LEUCHS (D.R.-P., 295246; addition to D.R.-P., 285344; from *J. Soc. Chem. Ind.*, 1917, **36**, 503).—A solution of crude zirconium oxide in hydrochloric acid is treated with sulphuric acid ($3ZrO_2 : 2H_2SO_4$) and left in the cold or at 40°. Zirconium sulphate separates in small prisms which are free from iron and also titanium. H. W.

The Zirconyl Bromides. ED. CHAUVENET (*Compt. rend.*, 1917, **164**, 816—818).—By the evaporation of a solution of zirconium hydroxide in hydrobromic acid on a water-bath, the hydrate of zirconyl bromide, $ZrOBr_2,8H_2O$ (compare Weibull, A., 1887, 778), was obtained. The author was unable to confirm the existence of the hydrates described by Knopp (compare *Annalen*, 1871, **159**, 36) and Paijkull (compare this Journal, 1873, 1105). The octahydrate when dried in a current of dry air or in a vacuum gives the hydrate $ZrOBr_2,3·5H_2O$, which is stable up to 60—70°. Above this temperature it loses water and hydrogen bromide, giving the compound $ZrOBr_2,ZrO_2$. This basic bromide is also slowly deposited from an *N*/100-solution of zirconyl bromide on long keeping. By the addition of ether to an alcoholic solution of zirconyl bromide, the *compound*, $ZrOBr_2,ZrO_2,12H_2O$, is obtained. In a current of hydrogen bromide at a red heat the basic bromide is converted into zirconium bromide, $ZrBr_4$. W. G.

Zirconium Fluorides and Zirconyl Fluorides. Ed. Chauvenet (*Compt. rend.*, 1917, **164**, 727—729).—The author considers that the substance, described in the literature as a hydrate of zirconium fluoride, $ZrF_4,3H_2O$, is really a hydrate of acid zirconyl fluoride, $ZrOF_2,2HF,2H_2O$. At 140° in dry air it loses two molecules of water, giving the anhydrous acid fluoride, which, when heated above 140° in air, loses two molecules of hydrogen fluoride, giving zirconyl fluoride, $ZrOF_2$; this, when cold, re-absorbs two molecules of hydrogen fluoride. The anhydrous normal zirconyl fluoride may also be obtained by crystallising the hydrated acid fluoride from dilute aqueous solution and drying the product, $ZrOF_2,2H_2O$, at 120°. If the anhydrous or hydrated acid fluoride is heated at 200° in an atmosphere of hydrogen fluoride, zirconium fluoride, ZrF_4, is obtained, which, in the cold, absorbs hydrogen fluoride, probably to form fluozirconic acid, H_2ZrF_6. W. G.

The Properties and Constitution of some New Basic Salts of Zirconium. Ernest Harry Rodd (T., 1917, **111**, 396—407).—From a basic zirconium sulphate of indefinite composition, precipitated by partly neutralising with ammonia an acid solution of zirconium sulphate, a new basic zirconium chloride, $Zr_5O_8Cl_4,22H_2O$, has been prepared. It is a crystalline salt, readily soluble in water, less so in hydrochloric acid solution, from which it can be recrystallised unchanged. The new 5 : 4 basic zirconium chloride is sharply distinguished from the common oxychloride, $ZrOCl_2,8H_2O$, by its property of forming with a solution of any sulphate an insoluble basic zirconium sulphate of corresponding composition, $Zr_5O_8(SO_4)_2,xH_2O$, x being about 14. From either the new basic chloride or sulphate can be prepared a new hydroxide, distinct from normal zirconium hydroxide in that, when dissolved in hydrochloric acid, it forms a solution of the new 5 : 4 basic chloride. By analogy, its composition is given as $Zr_5O_8(OH)_4$. It is suggested that the new salts have structural formulæ of the type $Zr(O\cdot ZrO\cdot Cl)_4$, which would account for the remarkable stability of the salts.

The changes undergone by a solution of zirconyl chloride when boiled are discussed (compare Ruer, A., 1905, ii, 41, 827), and also the formation of metazirconic acid. It is argued that the same property which leads to the formation of the many basic salts of zirconium eventually leads to the production of metazirconic acid. The hydrolysis of the salts in solution is followed by condensation of the hydrolysed molecules, with production of complex basic salts; when this process is pushed to the limit, metazirconic acid is formed. E. H. R.

The Compounds of Zirconium Oxide with Sulphuric Acid. Ed. Chauvenet (*Compt. rend.*, 1917, **164**, 864—865).—Mixtures of varying molecular proportions of zirconium oxide and sulphuric acid were made and dried at 200°, the densities of the resulting products being determined. The results obtained indicate the

existence of the six sulphates: $Zr(SO_4)_2$, $Zr(SO_4)_2,ZrO_2$, $5Zr(SO_4)_2,7ZrO_2$, $3Zr(SO_4)_2,5ZrO_2$, $Zr(SO_4)_2,2ZrO_2$, $Zr(SO_4)_2,3ZrO_2$.
W. G.

Enantiotropy of Bismuth. J. Würschmidt (*Jahrb. Min.*, 1917, i, *Ref.* 2; from *Festschrift Elster-Geitel*, 1915, 326—332).—The specific gravity of bismuth determined for a mass and for the powder is 9·80 and 9·70 respectively. This suggests that during the powdering the material passes over into a lighter modification, Bi_β, which is perhaps identical with that described by Cohen and Moesveld (A., 1914, ii, 779), and also recognised by the author in bismuth amalgam (A., 1916, ii, 517). L. J. S.

Osmium Dioxide. Otto Ruff and Hans Rathsburg (*Ber.*, 1917, **50**, 484—498).—The preparation and properties of various samples of osmium dioxide are described. The work was undertaken with the view of determining the atomic weight of osmium by reducing the oxide to the metal, but this has been abandoned owing to the difficulties.

Colloidal Solutions of Osmium Dioxide.—These solutions can be obtained by the reduction of alkali osmates with alcohol or by the hydrolysis of osmichlorides, thus: $K_2OsO_4 + 2H_2O + EtOH = OsO_2,2H_2O + 2KOH + C_2H_4O$; $K_2OsCl_6 + 4H_2O = OsO_2,2H_2O + 2KCl + 4HCl$. By the addition of sufficient quantities of electrolytes to the neutral solutions, the dioxide can be precipitated, but it forms a colloidal solution again when treated with acids, alkali hydroxides, or ammonia or washed free from electrolytes. Concentrated solutions appear black by reflected light or blue by transmitted light.

Pyrophoric Osmium Dioxide.—The oxide prepared by reduction or by the hydrolysis of ammonium osmichloride retains alkalis and organic substances very firmly. As a result, the dry powder is more or less dangerous to handle, as it may kindle on exposure to the air or detonate on warming. An old preparation, or one that has been warmed with water for some time with a view to its purification, will not be so dangerous, but then it will contain much free metallic osmium. The estimation of osmium as dioxide is therefore untrustworthy (see A., 1910, ii, 305).

Stable Osmium Dioxide.—An amorphous oxide containing about 1% of sodium chloride may be obtained by heating potassium osmichloride with pure sodium hydroxide solution in the absence of air. The dried powder corresponds with the formula $OsO_2,2H_2O$. One molecule of water is lost at 100° and the other at 200°, the residue being a bluish-black powder, D^{21} 7·71. The reaction of this oxide with hydrogen is almost explosive in its violence. Oxygen also reacts briskly, giving osmium tetroxide. When heated in an indifferent atmosphere, it becomes dark brown and decomposes at about 500° into osmium and osmium tetroxide. In an atmosphere of osmium tetroxide, however (partial pressure about 100 mm.), it may be heated to 640°, when it changes into a crystalline form, D^{22} 7·91. A copper-coloured sublimate (octahedra and hexahedra) is usually deposited on the tube, and it may be that the volatile oxide to which the formation of this sublimed dioxide is due is a trioxide, thus: $OsO_2 + OsO_4 \rightleftharpoons 2OsO_3$. The pure dioxide could be obtained by heating metallic osmium in an atmosphere of nitrogen and osmium tetroxide at 650°, but the pure metal must be as finely divided as possible. J. C. W.

Mineralogical Chemistry.

The Solvents of Coal. A. Wahl (*Bull. Soc. chim.*, 1917, [iv], **21**, 76—88).—An examination of the behaviour of different types of coal towards aniline and quinoline as solvents. The results obtained are in agreement with those of Vignon (compare A., 1914, ii, 570), Bedson (compare A., 1908, ii, 302), and Dennstedt and Bünz (compare *Zeitsch. angew. Chem.*, 1908, **21**, 1833). W. G.

Högbomite. Axel Gavelin (*Bull. Geol. Inst. Upsala*, **15**, 287—316; from *Chem. Zentr.*, 1917, i, 601).—The new mineral occurs in the iron ores in the neighbourhood of Ruoutevare (Lapland) associated with magnetite, ilmenite, pleonaste, corundum, and hydrargillite; it is hexagonal-rhombohedral, laminar, occasionally twinned toward the basis, very brittle, and conchoidal in fracture. The latter shows shining black, metallic particles which exhibit pleochroism similar to biotite. It is optically uniaxial, negative, and has ω 1·853, δ 1·803, hardness 6·5, D *ca.* 3·81. It is attacked by acids with difficulty, but, like pleonast and corundum, it is hydrated with loss of small amounts of TiO_2 and Fe_2O_3. Analysis (Mauzelius), after allowance for admixed ilmenite and pleonaste, gave:

TiO_2.	Al_2O_3.	Fe_2O_3.	Cr_2O_3.	MnO.	MgO.
5·33	61·19	17·41	0·29	0·14	15·44

This leads to the formula $RO,2R_2O_3$ if a portion of the R_2O_3 is replaced by TiO_2. Chemically, therefore, högbomite is a pleonaste in which the ferrous oxide is oxidised and partly replaced by titanium dioxide; in its physical properties it is most closely allied to the corundum–hæmatite group. H. W.

Leverrierite from Colorado. Esper S. Larsen and Edgar T. Wherry (*J. Washington Acad. Sci.*, 1917, **7**, 208—217).—The determination of the composition and the physical properties of the "clay-gouge" which occurs in the veins of quartz and pyrolusite at Beidell, Saguache Co., Colorado, has shown that this belongs to the leverrierite group. Analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O. (<110°).	H_2O. (>110°).	Total.
47·56	20·57	8·58	0·24	2·52	0·80	1·28	trace	6·65	12·01	100·21

These results are compared with those obtained for rectorite, leverrierite from Rochelle (France), batchelorite, kryptotile, and delanouite. These minerals show some variation in the water content and in the $SiO_2:Al_2O_3$ ratio, but the optical properties indicate that they belong to the same group and are probably related to the micas. H. M. D.

Staurolite. FRIEDRICH HÖRNER (*Jahrb. Min.*, 1917, i, *Ref.* 23—27; from *Inaug.-Diss., Heidelberg*, 1915, 41 pp.), E. A. WÜLFING, and F. HÖRNER (from *Sitzungsber. Heidelberg, Akad. Wiss., Math.-naturw. Kl.*, 1915, 11 pp.).—Detailed determinations were made of the crystallographic, optical, and other constants of staurolite from Pizzo Forno, St. Gotthard ($a:b:c = 0·4734:1:0·6820$; anal. I), Aschaffenburg, Bavaria (anal. II), and Petersdorf, Moravia (D 3·778). Staurolite is frequently rendered impure by the enclosure of quartz and other minerals, but the material analysed was quite pure. The analyses lead to the new formula $H_2O,4FeO,9Al_2O_3,8SiO_2$.

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	H_2O (at 110°).	H_2O (110—1000°).	Total.	Sp. gr.
28·08	0·73	51·90	1·80	13·39	2·08	0·11	1·62	99·71	3·753
27·68	0·77	53·37	2·33	12·69	1·78	0·13	1·46	100·21*	3·759

* Also MnO, trace ; CaO, nil.

L. J. S.

Scapolite-bearing Bombs from the Laacher See District. Refractive Indices of Sulphate-Scapolite. R. BRAUNS (*Jahrb. Min.*, 1917, i, 9—44).—A few more of the scapolite-bearing bombs are described in detail, and optical constants and analyses are given of the new member of the scapolite group, namely, sulphate-scapolite (A., 1915, ii, 836) or silvialite (R. Brauns, 1914). Analysis I is of colourless, transparent scapolite from a hornblende-scapolite-rock. This corresponds with $5[CaO,3CaAl_2Si_2O_8]$(meionite) + $4[CaSO_4,3CaAl_2Si_2O_8]$ (silvialite) + $2[CaCO_3,3CaAl_2Si_2O_8]$ (carbonate-meionite) + $2[NaCl,3NaAlSi_3O_8]$ (marialite) + $Na_2O,6NaAlSi_3O_8$ (chlorine-free marialite). Anal. II is of scapolite crystals from a felspar-hornblende-scapolite-rock, and corresponds with

$14[CaO,3CaAl_2Si_2O_8] + 8[CaSO_4,3CaAl_2Si_2O_8] + 5[Na_2O,6NaAlSi_3O_8]$; III of corroded scapolite from a hornblende-haüyne-scapolite-rock; and IV of the greyish-white grains of haüyne from the same rock; this agrees only approximately with the Brögger and Bäckström formula for haüyne, which is criticised. Analysis V is of the clear, fresh felspar from an anorthite-hornblende-scapolite-rock, and corresponds with $Ab_{15}An_{85}$.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	SO_3.	Cl.	H_2O. at 100°.	H_2O. >110°.	Total.	Sp. gr.
I.	43·98	29·99	0·59	18·35	0·14	2·73	0·67	2·28	0·49	—	0·21	100·07*	2·755
II.	46·59	26·33	1·31	15·70	0·52	3·68	1·11	2·06	trace	0·80		98·10	2·748
III.	44·04	28·48	0·92	18·72	0·18	2·97	0·25	2·06	—	0·04	2·09	99·87†	2·755
IV.	32·41	27·65	0·06	10·11	0·07	13·30	1·85	11·88	0·38	0·40	1·60	99·97‡	2·45—2·46
V.	45·70	33·93	0·92	17·22	0·09	1·77	0·20	0·11	—	0·32		100·31§	2·746

* Also CO_2, 0·64 ; TiO_2, MnO, traces. † Also TiO_2, 0·12. ‡ Also FeO, 0·26.
§ Also MnO, 0·05 ; BaO, trace.

L. J. S.

History of Chinese Mineralogy and Chemical Technology. H. J. Holgen (*Chem. Weekblad*, 1917, **14**, 468—476).—An account of early records of Chinese scientific investigations, and their application to industry. A. J. W.

Analytical Chemistry.

Reducing Matter Extractable from Filter Paper. R. S. McBride and J. A. Scherrer (*J. Amer. Chem. Soc.*, 1917, **39**, 928—933).—The authors show that when solutions, to be estimated volumetrically by means of potassium permanganate, have to be filtered before titration, the results are somewhat high owing to the washing out of a reducing substance from the paper by means of the reagents. To ascertain the amount of this substance and the dimensions of the error introduced, a number of experiments have been made with various types of filter papers. The experiments were made by running quantities of various reagents of 250 c.c. in each case through the paper; the filtrate was then coloured with 0·03 c.c. of $N/10$-potassium permanganate, and the time required for the solution to become colourless compared with the time required in a blank. Solutions of sulphuric acid ($2\frac{1}{2}$ and 5%), sodium hydroxide (1%), and sodium carbonate (2%) were used. In every case, whether the solutions were filtered hot (70°) or cold, the permanganate is reduced much more rapidly than in the blank experiments. It is shown that a comparatively small volume of the reagent removes the reducing substance which is not reformed. Maceration of the paper with the reagent does not give any more of the reducing substance, even although the titration is carried out in the presence of the paper pulp. Old filter papers have just the same action as new ones. It is suggested that a preliminary washing of the filter paper with the reagent will remove all source of error. The reducing substance is probably furfuraldehyde.

J. F. S.

Improvement in the Use of the Gooch Crucible. Ernst Korten (*Chem. Zeit.*, 1917, **41**, 267).—The washing of precipitates in a Gooch crucible is facilitated by means of a glass, dome-shaped cover which is fixed on the crucible by a rubber band; a tube passes through the top of the cover and extends into the upper part of the crucible, the part of the tube above the cover being bent downwards and either connected with a wash-bottle or dipped into water contained in a beaker. The crucible is connected with a suction pump in the ordinary way, and the flow of water into the crucible is regulated by a tap and screw-clip. W. P. S.

Methyl-red [as an Indicator]. F. Lehmann and G. Wolff (*Arch. Pharm.*, 1917, **255**, 113—119).—Methyl-red (*p*-dimethylaminoazobenzene-*o*-carboxylic acid) has about the same universal value as an indicator for the titration of bases of all strengths that phenolphthalein has for acids. That is, it is more sensitive to hydroxyl ions than is methyl-orange. It is also more sensitive towards hydrogen ions (compare Fels, A., 1910, ii, 320), and might therefore be of more extended use than methyl-orange in acidimetry, but probably of less use in the titration of salts of strong bases with weak acids. This has now been tested, and it is found that oxalic and picric acids can be titrated readily with it, and also alkali borates and cyanides, whilst sulphites do not give sharp end-points, and sulphides and carbonates give intermediate orange tones which should be ignored and the final change to bright pink waited for. The change from red (acid) to yellow (alkaline) is as sharp as the change from yellow to red, and solutions standardised against phenolphthalein are practically of the same normality with regard to methyl-red. The best results are obtained with two or three drops of a 0·1% solution in about 100 c.c. of liquid.

J. C. W.

Handling a Standard Solution of Barium Hydroxide. W. G. Haynes (*J. Ind. Eng. Chem.*, 1917, **9**, 58—59).—In order to avoid the use of rubber tubing to connect the syphon tube of the barium hydroxide reservoir with the burette, a glass valve may easily be constructed out of a T-tube and a glass rod of such thickness that it slides smoothly in the longer arm of the T. The latter is closed at one end to a small hole one or two millimetres in diameter, and the glass rod, rounded off, is ground into the partly closed end of the T-tube to make a tight joint. The syphon tube is then connected with the free arm of the T, the glass rod bent round twice at right angles and held in position by a weak spring, and the whole is fixed by means of a rubber stopper in the top of the burette. A slight upward pressure on the glass rod opens the aperture in the T-tube and allows the hydroxide solution to flow between the rod and the sides of the tube into the burette.

G. F. M.

Yellow Mercuric Oxide as a Standard in Alkalimetry. G. Incze (*Zeitsch. anal. Chem.*, 1917, **56**, 177—191).—Yellow mercuric oxide is readily prepared in a pure state, is anhydrous and non-hygroscopic, and is a trustworthy substance for use in standardising acid solutions, since it yields an equivalent quantity of alkali hydroxide when treated with potassium iodide: $HgO + 4KI + H_2O = K_2HgI_4 + 2KOH$. For use, a weighed quantity of about 0·4 gram of the oxide is mixed with 10 c.c. of 60% potassium iodide solution and, as soon as the oxide has dissolved, the mixture is titrated with the acid solution to be standardised, using methyl-orange, methyl-red, or phenolphthalein as the indicator.

W. P. S.

Valuation of Bromides. E. Rupp and E. Hollatz (*Arch. Pharm.*, 1917, **255**, 120—129).—The authors have developed a titrimetric method for the estimation of bromides in the presence of small quantities of chlorides, which is designed especially for the valuation of pharmaceutical preparations, such as *Bromum compositum*, D.A.-B. ($KBr:NaBr:NH_4Br$, 2:2:1). The process is summarised in the following equations: $5KBr + KBrO_3 + 6H_2SO_4 = 3Br_2 + 6KHSO_4 + 3H_2O$; $Br_2 + 2NaOH + H_2O_2 = 2NaBr + O_2 + 2H_2O$; $KBrO_3 + 6KI + 6H_2SO_4 = 3I_2 + 6KHSO_4 + KBr + 3H_2O$.

The reason for removing the bromine by the application of alkaline hydrogen peroxide, rather than by boiling, is that the excess of bromate is not stable in hot acid solutions. Ammonium salts tend to produce bromates at this stage, however, so the first step is really to expel any ammonia by boiling with sodium hydroxide. The solution is then cooled, acidified, treated with a definite excess of bromate, then mixed with alkaline hydrogen peroxide, and, after boiling, acidifying, and adding potassium iodide, the iodine is titrated by thiosulphate. Sufficiently trustworthy results are obtained even if the mixture contains as much as 25% of a chloride.

J. C. W.

Estimation of Oxygen in Blood. D. D. VAN SLYKE (*Proc. Soc. Exp. Biol. and Med.*, New York, 1917, **14**, 84—85; from *Physiol. Abstr.*, 1917, **2**, 178).—The estimation can be made in five minutes by means of the author's apparatus for the estimation of carbon dioxide. After complete extraction of air from the apparatus and reagents, 2 c.c. of blood are laked with dilute ammonia solution and allyl alcohol. The oxygen is liberated by shaking with 0·5 c.c. of air-free, saturated potassium ferricyanide solution in a vacuum, and is estimated precisely as is carbon dioxide. The only correction needed is for the small amount of nitrogen gas present in blood.

G. B.

Estimation of Sulphur in Pyrites. C. ZAY (*Stat. sperim. agrar. ital.*, 1916, **49**, 530—536; from *Chem. Zentr.*, 1917, i, 446). —Finely powdered pyrites (1 gram) is treated in a covered porcelain dish with a cold mixture of nitric acid (20 c.c.) and concentrated hydrochloric acid (5 c.c.); when the reaction has subsided, the solution is evaporated to dryness, the residue moistened with hydrochloric acid (5 c.c.), again evaporated to dryness, and subsequently dissolved in a mixture of water (100 c.c.) and hydrochloric acid (1 c.c.). The iron is precipitated by ammonia (D 0·91, 10 c.c.) and the mixture warmed for ten minutes at 60—70°. The precipitate is filtered and the filtrate brought to 250 c.c. by washings of the precipitate (solution *A*). The ferric hydroxide is dissolved in the minimum quantity of concentrated hydrochloric acid, the solution diluted to about 175 c.c., the iron again precipitated, and the filtrate brought to 250 c.c. (solution *B*). One hundred c.c. of each of the solutions *A* and *B* are neutralised with dilute hydrochloric acid in the presence of methyl-orange and, after addition of hydrochloric acid (1 c.c.), precipitated at the boiling point with barium chloride solution (3%, 100 c.c.). After remaining for half an hour, the solution is decanted, the precipitate washed four times by decantation with boiling water (100 c.c.), filtered, and washed until

5 c.c. of the filtrate do not give a turbidity when mixed with 5 c.c. of dilute sulphuric acid. The precipitate is subsequently dried and ignited. H. W.

Estimation of Total Nitrogen. G. H. G. Lagers (*Chem. Weekblad*, 1917, **14**, 492—499).—A comparative study of methods for estimating nitrogen in manures, including those of Kjeldahl, Schlœsing, and Jodlbaur, and the distillation method. A. J. W.

The Phenoldisulphonic Acid Method for Estimating Nitrates in Soils. Charles W. Davis (*J. Ind. Eng. Chem.*, 1917, **9**, 290—295).—The accuracy of the usual method of applying phenoldisulphonic acid for the estimation of nitrates in soils is not affected by the presence of ammonia in the atmosphere during the operation, or by the manner in which the acid is added, whether with or without stirring, or by the temperature of the solution at the time alkali is added to develop the colour, except that at 0° a loss (4 parts per million in a 100 part per 1,000,000 solution) was noted. Light, however, affects the colour, and the reading should be made without delay. Loss of nitrates was found to occur during the evaporation on the water-bath, notably when chlorides and sulphates were present, but carbonates, acetates, and salts of weak acids generally produced no accentuation of the loss. A maximum loss of 30% of the nitrate present was observed when uniform amounts of phenoldisulphonic acid were used with increasing proportions of nitrate. By evaporating the solutions to dryness with a slight excess of calcium hydroxide, all loss was prevented, even in the presence of chlorides and sulphates, provided that care was taken also to flood an excess of the sulphonic acid reagent quickly over the residue; otherwise the hydrochloric acid generated when chloride is present may lead to the escape of nitric acid. Potassium alum may be used as a flocculent in preparing the soil solution without causing loss of nitrate, provided the modified method of procedure is employed, and it is recommended as superior to copper sulphate and other flocculents for this particular purpose. G. F. M.

Estimation of Phosphorus in Zinc Phosphide. G. Liberi (*Ann. Chim. Applicata*, 1917, **7**, 144—151).—The estimation of phosphorus in phosphides by oxidation to phosphate by means of nitric acid or aqua regia is not applicable to phosphides which are readily attackable by dilute hydrochloric or sulphuric acid, since with these the oxidation is only partial. This is the case with zinc phosphide, which, however, liberates its phosphorus quantitatively as hydrogen phosphide when treated with dilute sulphuric acid (1 vol. of the acid to 2 vols. of water). The method of estimation proposed by the author depends on this reaction, which is carried out in a current of carbon dioxide and occurs largely in the cold; when the reaction slackens, the liquid is gently boiled for half an hour, the flame being then extinguished and the carbon dioxide kept flowing for another half an hour. The hydrogen phosphide formed is absorbed by 50 c.c. of a neutral 3% silver nitrate solution contained in a 7- or 10-bulbed tube, this being followed by a Péligot tube containing 10 c.c. of the solution, which serves as a check and should remain clear. The bulbed tube is emptied into a beaker together with the nitric acid and water used to rinse it out, and the whole gently heated on a water-bath until the precipitate completely dissolves. The silver is then precipitated with a slight excess of hydrochloric acid and the liquid evaporated almost to dryness, diluted again with water, filtered, and washed. In the filtrate the phosphoric acid is precipitated in the hot as ammonium magnesium phosphate and weighed after ignition as magnesium pyrophosphate. The result obtained in this way represents the active phosphorus.

If the total phosphorus, including that present in the phosphide as phosphate, is required, the following method may be used. The substance (0·2—0·3 gram) is introduced into a flask fitted with a tapped funnel and a delivery tube connected with a Péligot tube containing 10 c.c. of the 3% silver nitrate solution, the flask having been previously filled with carbon dioxide. About 10 c.c. of water are introduced through the funnel and then 50 c.c. of the silver nitrate solution, the flask being shaken. Nitric acid is next gradually added and the liquid heated until solution is complete, the flame being then extinguished and the current of carbon dioxide continued for fifteen minutes longer. The Péligot tube serves also in this case to indicate if there is any slight escape of hydrogen phosphide; if its contents show any brown coloration, they are subsequently added to the main liquid in the flask. Owing to the presence of dissolved zinc and silver, the phosphate must first be precipitated as ammonium phosphomolybdate.

Zinc phosphide should not contain more than very small proportions of arsenic. T. H. P.

Estimation of Phosphoric Acid and Phosphates by Alkalimetric Methods. John H. Smith (*J. Soc. Chem. Ind.*, 1917, **36**, 415—419).—Attempts to titrate solutions of phosphoric acid with *N*/1-sodium hydroxide at the ordinary temperature in the presence of methyl-orange, methyl-red, and phenolphthalein respectively show that the generally accepted points of neutrality with the first- and third-named indicators are only approximately correct; the end-points are, however, quite regular and fairly definite, so that correct results may be obtained by using certain factors. If the titrations are accomplished at 55°, however, accurate results are obtained without the use of factors.

For the analysis of phosphates, 5—6 grams of the sample are dissolved in the minimum quantity of distilled water and two drops of phenolphthalein are added; if the solution is not coloured pink, the absence of Na_3PO_4 and Na_2CO_3 may be assumed. The solution is heated to 55° and titrated at this temperature with *N*-sodium hydroxide solution until a pink coloration is noticeable. The determination of the end-point requires a certain amount of practice and is facilitated by the presence of sodium chloride. The solution is next titrated back with *N*-hydrochloric acid with addition of a few drops of methyl-orange solution. Sufficient data are thus obtained if it is known that the solution contains only $Na_2HPO_4 + NaH_2PO_4$ or $NaH_2PO_4 + H_3PO_4$. In order to make the method uniform, however, the author prefers to add a further quantity of *N*-hydrochloric acid (about equal to that previously employed) to the solution, which is then boiled vigorously for at least fifteen minutes, whereby carbonates are decomposed and any metaphosphoric acid or metaphosphate is converted into the ortho-form; after being cooled to 55°, the excess of acid is neutralised by *N*-sodium hydroxide at first to the disappearance of the methyl-orange pink and finally to the appearance of the phenolphthalein pink. If now the last end-point corresponds with the original end-point, the possibility of the presence of metaphosphoric acid and its salts as well as of carbonates in the original substance is excluded. For full details with regard to calculations, the original memoir should be consulted.

When all precautions are taken, results within 0·5% of accuracy are obtained.

When metaphosphate is known to be present, *N*-sulphuric acid should replace *N*-hydrochloric acid and the solution should be evaporated to dryness after boiling to ensure the complete conversion of the meta- into the ortho-form; otherwise, however, it is preferable to employ hydrochloric acid. H. W.

Detection of Arsenic by means of Mercuric Chloride Paper. L. Vuaflart (*Ann. Falsif.*, 1916, **9**, 446—448).—The advantages of the Gutzeit test are discussed. As applied to certain samples of "glucose" containing large quantities of arsenic, the method gave higher but more trustworthy results than did the Marsh test. The interfering action of sulphites, which are sometimes present in "glucose," may be overcome by precipitating the arsenic as ammonium magnesium arsenate and then testing the precipitate. W. P. S.

Arsenic Trisulphide. Ernst Schmidt (*Arch. Pharm.*, 1917, **255**, 45—64).—A description of tests which have been made as to the behaviour of precipitated arsenious sulphide towards various liquids. It is found that the sulphide is appreciably decomposed by water and even by alcohol with formation of hydrogen sulphide. It is also attacked to a very considerable extent by dilute hydrochloric acid, but the action with dilute acid or with water is checked by the addition of a small quantity of hydrogen sulphide.

The estimation of arsenic by precipitation and weighing as trisulphide (Puller, this Journal, 1871, **24**, 971; Friedheim and Michaelis, A., 1896, ii, 74) gives results which are very slightly high, but actually the precipitate diverges more widely from the composition As_2S_3 than the errors would indicate, containing to some extent both arsenic hydrosulphide, $As(SH)_3$, and arsenious oxide, the respective errors being in opposite directions and tending to equalise each other.

A slightly modified method is suggested for the treatment of precipitated arsenic sulphide in order to convert it into an arsenious solution suitable for titration with iodine. D. F. T.

Carbon Dioxide Absorption Apparatus. L. G. Wesson (*J. Ind. Eng. Chem.*, 1917, **9**, 59).—A new carbon dioxide absorption apparatus for organic combustions consists of a cylindrical bulb of thin glass containing moist soda-lime, connected near the base by means of a thick-walled capillary tube with a small vertical side-arm sufficiently large to hold about 7 grams of calcium chloride. Both necks of the apparatus are provided with ground-in stopcocks, and the whole when empty weighs only 20 to 25 grams. G. F. M.

Estimation of Carbon Dioxide in Water. J. Tillmans and O. Heublein (*Zeitsch. Nahr. Genussm.*, 1917, **33**, 289—304).—Free carbon dioxide and that present as hydrogen carbonates in water cannot be estimated accurately by precipitation with barium hydroxide and titration of the excess of the latter after the barium carbonate has settled; the inaccuracy of this method is due to the occlusion of barium hydroxide in the precipitated carbonate. The method is applicable, however, to solutions of carbon dioxide and hydrogen carbonates in distilled water provided that the whole mixture (liquid and precipitate) is titrated, using phenolphthalein as indicator; the presence of magnesium salts renders this modification useless in the case of many drinking waters. The free carbon dioxide in water may be estimated by adding 1 c.c. of 0·0375% phenolphthalein solution to 200 c.c. of the water contained in a stoppered flask and then titrating the solution with *N*/20-sodium hydroxide solution until a pink coloration is obtained which persists for five minutes. If, at the end of the titration, the solution contains more than 440 mg. of carbon dioxide in the form of hydrogen carbonate, the estimation must be repeated after the sample has been diluted with water free from carbon dioxide. Winkler's method (A., 1915, ii, 281) is considered to be untrustworthy. W. P. S.

Accurate Estimation of Silica in Commercial Analysis. F. G. Hawley (*Eng. and Min. J.*, 1917, **103**, 541—543; from *J. Soc. Chem. Ind.*, 1917, **36**, 521).—Attention is directed to sources of error in the estimation of silica due to the solubility of silica in hydrochloric acid, the presence of silica in the fusion mixture itself, and to impurities retained by the washed silica. The solubility of the silica, which may amount to 2% in samples containing less than 20% of silica, may be diminished by heating the saline residue at 150° during thirty minutes, then adding 15 c.c. of hydrochloric acid (60%), heating the mixture to boiling for three minutes, and collecting the silica on a filter, where it is washed successively with water, dilute hydrochloric acid, and water. To estimate silica in ores containing much lead, copper, antimony, etc., the ore may be fused in a nickel crucible with a mixture of sodium hydroxide and sodium peroxide (equal parts by weight), followed by the above method of separation. Under these conditions, the loss of silica by solution is about 0·4%, but this loss is balanced approximately by impurities in the silica and the quantity of the latter derived from the fusion mixture. H. W.

Detection of Calcium in the Presence of Barium and Strontium. Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1917, **56**, 138—141).—The test described depends on the insolubility of calcium fluoride and the relative solubility of barium fluoride and strontium fluoride. One litre of water dissolves 16 mg. of calcium fluoride, 117 mg. of strontium fluoride, or 1630 mg. of barium fluoride. Barium fluoride solution is used as the reagent. A distinct turbidity is produced when this solution is added to 10 c.c. of water containing 0·0008 gram of calcium (as chloride). The presence of strontium chloride or ammonium chloride in the calcium chloride solution does not affect the sensitiveness of the reaction, but it is decreased when barium chloride is present. W. P. S.

Estimation of Zinc by Schaffner's Method. W. ORLIK (*Zeitsch. anal. Chem.*, 1917, **56**, 141—144).—A reply to Patek's criticism of this method (A., 1916, ii, 578). W. P. S.

Estimation of Zinc. J. H. HASTINGS (*Met. and Chem. Eng.*, 1917, **16**, 263—265; from *J. Soc. Chem. Ind.*, 1917, **36**, 506).—Solution of the ore and separation of iron and manganese are effected as usual, the zinc being determined by titration with standard potassium ferrocyanide in a boiling, slightly acid solution (volume about 200 c.c. containing 5 c.c. excess of hydrochloric acid) containing hydrogen sulphide, a saturated aqueous solution of which (50 c.c.) is added to prevent decomposition of the ferrocyanide by oxidising agents and to precipitate any small quantity of copper present. A solution of uranium nitrate (5%) is used as external indicator. H. W.

Analysis of Antimonial Lead. C. R. McCABE (*J. Ind. Eng. Chem.*, 1917, **9**, 42—44).—The method adopted is that of Demorest (A., 1913, ii, 982), modified with the object of freeing the precipitate of lead sulphate from antimonial contamination. One gram of alloy is dissolved completely in 50 c.c. of concentrated sulphuric acid, finally boiling for five minutes to oxidise the tin. On dilution with water, lead sulphate is precipitated, and, after boiling, the precipitate is collected, dissolved in a 20% solution of ammonium acetate, and reprecipitated with sulphuric acid. It is then quite free from antimony, and may be collected on a Gooch crucible, and weighed. Antimony is determined in the two filtrates separately by titration with permanganate and ferrous sulphate, and tin in the first filtrate by the iron reduction and iodine titration method. G. F. M.

Electrolytic Analysis with Small Platinum Electrodes. F. A. GOOCH and MATSUSUKE KOBAYASHI (*Amer. J. Sci.*, 1917, [iv], **43**, 391—396. Compare A., 1912, ii, 986).—Slight alterations are made in the apparatus described previously (*loc. cit.*), so that the small electrodes may be used with volumes of solution similar to those usually employed in electrolytic analysis. The rotating electrode consists of a piece of platinum gauze, 1—2 cm. square, into the central meshes of which is fused the tapered end of a lead-glass rod; a length of platinum wire is twisted round the glass rod and serves for making the electrical connexion. The stationary electrode is a strip of thin platinum foil, 5 cm. by 0·5 cm., welded to a connecting wire and suspended in a thin glass beaker of about 120 c.c. capacity. A small filtering tube, for collecting disengaged particles of deposited metal, is made by fusing the end of a lead-glass tube to a disk of platinum gauze and coating the disk with a layer of asbestos. The beaker, both electrodes, and the filtering tube are weighed together before use. The apparatus may be used for the estimation of copper, nickel, and lead. W. P. S.

Electroanalysis using Silvered Glass Basins in place of Platinum Cathodes. JUL. GEWECKE (*Chem. Zeit.*, 1917, **41**, 297—298).—The silvered basins are prepared as follows. A glass basin of about 100 c.c. capacity has its inner surface ground (this is best effected by means of a sand-blast, but etching with hydrofluoric acid may be used, although the surface produced is sometimes irregular), the basin is then treated with hot sulphuric acid and potassium dichromate, sodium hydroxide, nitric acid, and water, and is next nearly filled with a mixture consisting of 100 c.c. of silver nitrate solution and 2 c.c. of 40% formaldehyde solution; the silver nitrate solution is prepared by dissolving 8·5 grams of silver nitrate in 100 c.c. of water, adding ammonia until the precipitate first formed is nearly dissolved, filtering the mixture, and diluting the filtrate to 1 litre. The formaldehyde is added immediately before the mixture is poured into the basin, and in about four minutes the silvering is completed; the basin is then emptied, washed with water and alcohol, and dried. The temperature of the silvering solution should not exceed 30°, or the silver coating will be unequal. A thin strip of platinum foil is now bent over the edge of the basin so that its lower edge touches the silver coating, and the basin is weighed. A vulcanite screw clip is used for connecting the platinum strip with the negative pole of the source of electricity; a platinum anode is employed. The apparatus may be used for the electrolytic estimation of copper, cadmium, zinc, nickel, and cobalt. W. P. S.

The Hydrogen Peroxide Reaction for Copper and the Hydrolytic State of Dilute Copper Sulphate Solutions. FRIEDRICH MAYER and W. H. SCHRAMM (*Zeitsch. anal. Chem.*, 1917, **56**, 129—138. Compare A., 1907, ii, 549; 1916, ii, 314).—A *N*/10,000-copper sulphate solution yields a distinct reaction with hydrogen peroxide, and even smaller quantities of the metal can be detected. The addition of sodium hydrogen carbonate increases the sensitiveness of the reaction. It is shown that in very dilute copper solutions a portion of the copper is present as the hydrosol of copper oxide. W. P. S.

Analysis of Babbit Metal. J. C. WITT (*Philippine J. Sci.*, 1916, **11**, [*A*], 169—175).—The following methods are recommended for alloys having the composition: lead, 85—90%; antimony, 10—15%; tin, 0—5%; and copper, 0—1%. *Antimony.*—This metal may be estimated by a modification of Low's method (A., 1907, ii, 304); the alloy is dissolved in sulphuric acid, the solution boiled with the addition of hydrochloric acid, then cooled, diluted, and titrated with potassium permanganate solution. *Tin.*—The alloy is decomposed with sulphuric acid, the solution then diluted, heated with hydrochloric acid and steel turnings in a current of carbon dioxide, and, when all the turnings have dissolved, the mixture is cooled and titrated with *N*/10-iodine solution; the steel turnings used should be as free as possible from phosphorus. *Lead.*—The tin is first separated by treating the alloy with nitric acid, the lead is then precipitated as sulphate; this is collected, washed, dissolved in hot ammonium acetate solution, and the solution is titrated with ammonium molybdate solution, using tannin solution as an external indicator. The ammonium molybdate solution is standardised against pure lead under the same conditions. *Copper.*—The alloy is decomposed with nitric acid, then treated with an excess of ammonia, and the copper is estimated colorimetrically. *Iron and Zinc.*—The filtrate from the lead sulphate is heated, treated with hydrogen sulphide, and any precipitate which forms is separated by filtration; the solution is then oxidised by boiling with the addition of nitric acid and the iron is precipitated as hydroxide; the zinc is estimated in the filtrate from the ferric hydroxide. It is convenient to prepare a set of standard Babbit metals for use in standardising the reagents used in the analysis. W. P. S.

Analysis of Aluminium Dust. J. E. CLENNELL (*Eng. and Min. J.*, 1917, **103**, 496—499; from *J. Soc. Chem. Ind.*, 1917, **36**, 506).—The sample (1 gram) is dried at 100° until constant in weight and the loss reported as moisture. The dried material is treated with ether, the filtered extract being evaporated in a tared flask and the grease weighed. The residue from the extraction is transferred to a 300 c.c. flask and dissolved in dilute hydrochloric acid; the hot acid solution is filtered through the filter previously used into another flask and the filter washed with hot water. The insoluble residue is washed back and treated with nitric acid; this solution is passed through the same filter into a separate flask. The ignited, insoluble residue consists of silica mixed with some carbon which persistently resists ignition. It is fused with a small quantity of sodium peroxide and the silica separated as usual; this is calculated to silicon. The nitric acid filtrate is evaporated with sulphuric acid and added to the main hydrochloric acid filtrate.

This is precipitated with hydrogen sulphide and the precipitate digested with hot hydrochloric acid (50%) to separate copper and lead. The residual copper sulphide is dissolved in nitric acid and the copper titrated with cyanide. The lead solution is neutralised with ammonia, acidified with acetic acid, and precipitated with dichromate. The filtrate from the hydrogen sulphide precipitate is oxidised and treated with an excess of sodium hydroxide; the precipitate is dissolved and reprecipitated with ammonia; the filtrate from the ferric hydroxide is used for the estimation of magnesium. The alkaline filtrate containing aluminium and zinc is precipitated with sodium sulphide and the zinc sulphide estimated with *N*/10-iodine and thiosulphate. The aluminium may be roughly estimated by acidifying the last filtrate, expelling hydrogen sulphide by boiling, making up to 500 c.c., and titrating 100 c.c. with *N*/1-alkali first with methyl-orange, and then with phenolphthalein as indicator. The interval between the two end-points is proportional to the aluminium; the alkali is standardised against pure aluminium. Special methods for the separate estimation of the impurities are also described. H. W.

Micro-diagnosis of a Jadeite Chisel. ALOIS CATHREIN (*Jahrb. Min.*, 1917, 1, *Ref.* 20—22; from *Zeitschr. F~~erdinandeums,~~ Innsbruck*, 1915, [iii], **59**, 241—251).—The material of a pale green stone chisel, D 3·34, from Mt. Bondone, Trent, Tyrol, was identified as jadeite by the following method—called a 'micro-tachy-method,' being quick and applicable to small amounts of material. A small chip is crushed for the determination of the optical characters under the microscope. The same powder is afterwards used for determining the fusibility and flame coloration, the intensity and duration of the flame giving some idea of the percentage of sodium, etc. A 'volumetric' analysis performed in the wet way in narrow tubes of the same gauge gives, from the volumes of the various precipitates, an approximation to the quantitative composition. Silicates are decomposed by hydrofluoric acid, and the precipitates are separated and washed by decantation. Control experiments on known substances are performed when necessary.

L. J. S.

Stripping and Analysis of Galvanised Iron. GEORGE W. HEISE and AMANDO CLEMENTE (*Philippine J. Sci.*, 1916, **11**, [*A*], 135—146).—Separation of the zinc from the iron may be effected by phosphoric acid, sodium hydrogen sulphate, hydrochloric acid, or sulphuric acid; acetic acid may also be used, but the action is slow. Further, the separation can be made by means of solutions of certain lead, cadmium, copper, cobalt, chromium, and aluminium salts. Stripping and analysis can be effected by the electric current by making the galvanised plate the cathode in sulphuric acid solution, or the anode in concentrated alkali hydroxide solution, or in an oxidising solution (for example, sodium nitrate solution). In any of these methods, the amount of iron removed, together with the zinc from the plate, is mainly that contained in the zinc–iron alloy present in the coating, and is not due to corrosion of the iron plate itself. W. P. S.

Testing of Galvanised Iron. J. C. WITT (*Philippine J. Sci.*, 1916, **11**, [*A*], 147—165).—The zinc coating on galvanised plates may be separated and its quantity estimated by immersing a piece of the plate, 15 cm. by 15 cm., for about ten minutes in hydrochloric acid (D 1·098) at 45°, and then re-weighing the plate after it has been washed and dried. The small quantity of iron which is dissolved by the acid may be estimated by titrating the solution with permanganate solution. Measurements of the solution-velocity of galvanised iron indicate that the system of zinc–iron alloys is very complex; from the solution–velocity time curves an approximate idea of the uniformity and purity of the zinc coating may be obtained. W. P. S.

Estimation of Chromium in Ferrochrome. KOCH (*Stahl & Eisen*, 1916, **36**, 1093; from *Chem. Zentr.*, 1917, i, 532. Compare Herwig, this vol., ii, 104).—In the analysis of ferrochrome rich in chromium the author controls the permanganate titre with *N*/10-potassium dichromate and has up to the present observed no discrepancies with the titre calculated from the iron factor 0·3109. H. W.

Estimation of Chromium in Ferrochrome. G. SCHUMACHER (*Stahl & Eisen*, 1916, **36**, 1093—1094; from *Chem. Zentr.*, 1917, i, 532. Compare Herwig, this vol., ii, 104).—In the estimation of chromium by Phillips's method, the author has also obtained too low results for the chromium titre according to the usual methods of calculation. The discrepancies are greater than those observed by Herwig. H. W.

Chemical Evaluation of Alkali Chromates and Dichromates. J. F. SACHER (*Farbenzeitung*, 1916, **22**, 213; from *Chem. Zentr.*, 1917, i, 693).—The following method is sufficiently accurate for technical purposes and permits the estimation of chromate in presence of dichromate. Potassium dichromate can be titrated with potassium hydroxide in the presence of phenolphthalein in accordance with the equation $K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$. The titration can be performed without the indicator, since, at the neutral point, the colour of the solution changes from reddish-yellow to greenish-yellow. Potassium chromate can be estimated by titration with sulphuric acid according to the scheme $2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O$; Congo-red can be used as indicator. H. W.

Detinning and Analysis of Tin Plate. GEORGE W. HEISE and AMANDO CLEMENTE (*Philippine J. Sci.*, 1916, **11**, [*A*], 191—199). —The tin coating is most satisfactorily separated from tin plate by means of an electric current, the plate being made the anode in a 30% sodium nitrate solution; the iron plate is not attacked under these conditions. The tin may also be removed by immersing the plate in lead acetate solution rendered alkaline with sodium hydroxide. W. P. S.

A New Industrial Apparatus for the Estimation of Combustible Cases. Enrique Hauser (*Anal. Fis. Quim.*, 1917, **15**, 146—162. Compare this vol., ii, 266).—A critical survey of the effect of the experimental conditions on the accuracy of the results obtained with the author's eudiometer, and a comparison of these results with those derived by the aid of other types of apparatus. A. J. W.

The Estimation of Gasolene Vapour in Air. R. P. Anderson (*J. Ind. Eng. Chem.*, 1917, **9**, 142).—The apparent complete agreement in the figures obtained by Burrell and Robertson (A., 1915, ii, 184) for the estimation of gasolene vapour in air by the combustion and liquid air condensation methods is due in the case of the higher percentages to the approximate method of computing the results of the combustions. When high percentages of gasolene are present (that is, over 5 or 6%), combustion is incomplete and the figures obtained are considerably below the truth.
G. F. M.

Approximate Estimation of Toluene and Benzene in Coal Tar Oils. George Harker (*J. Roy. Soc. New South Wales*, 1916, **50**, 99—105).—The oil is distilled from an ordinary distillation flask, the fraction boiling below 170° is collected, washed with sulphuric acid and with sodium hydroxide solution, and then distilled at the rate of 1 drop per second from a round-bottomed flask fitted with a Young and Thomas five-section still-head. The volume of distillate collected below 95° is approximately equivalent to the amount of benzene present, and the distillate collected between 95° and 130° gives the amount of toluene. The quantities of benzene and toluene are then checked by adding to the residue in the flask quantities of pure benzene and toluene in accordance with the amounts found in the preliminary distillation, and redistilling this mixture. Any error in the first estimation is thus corrected. W. P. S.

Analysis of Light Oils [for Benzene, Toluene, and Xylene]. G. Egloff (*Met. and Chem. Eng.*, 1917, **16**, 259—263; from *J. Soc. Chem. Ind.*, 1917, **36**, 498—499).—The still consists of a copper flask of 4000 c.c. capacity, provided with a fractionating column 2·4 m. high and a condenser 0·6 m. long. The column is made up of six 0·3 m. and one 0·45 m. lengths of 18 mm. and one 0·15 m. length of 36 mm. iron pipe connected by suitable unions; it has a reflux tube (9 mm. diam.) which extends through the lowest section of the column to within 25 mm. of the bottom of the flask when the latter is screwed into position. The reflux tube communicates with the main column at intervals, and the different sections of the column are separated by diaphragms of 30-mesh iron wire gauze, each of which supports an 0·2 m. column of glass rods 50 mm. long and 12 mm. in diameter. The head of the column is provided with a thermometer and pipe connected to the condenser. The heating burners and, if necessary, the column are screened from draughts. Experiments with known mixtures of benzene, toluene, and xylene, distilled at the rate of 2 drops per second, gave results in close agreement with the theoretical, the loss being very small. In the case of various commercial oils, a much better separation of benzene, toluene, and xylene was effected by a single distillation in this apparatus than by three successive fractionations with a standard Hempel column.

For analysis, the oil (2000 c.c.) contained in a vessel provided with a cooling coil and stirring apparatus, is agitated for about eighty minutes with sulphuric acid (200 c.c., 95%), added at the rate of about 1 drop per second, and the mixture left for thirty minutes; the acid sludge is then discharged and the remaining oil, now free from olefines, agitated for fifteen minutes with a solution of sodium hydroxide (6%) and allowed to remain for thirty minutes. After separation from the alkali sludge, the oil is distilled with live steam until the temperature reaches 180°. The oil is then separated from the distillate and, after thorough drying with calcium chloride, distilled in the apparatus described, the fractions boiling up to 95°, between 95° and 125°, and between 125° and 165° being collected, measured, and recorded as pure benzene, toluene, and solvent naphtha unless the specific gravities fall below 0·880, 0·871, and 0·870 respectively, when the presence of paraffins is indicated. In the latter case the proportion of paraffins present is calculated on the basis of the wide difference in specific gravity between paraffin and aromatic hydrocarbons distilling over the same range of temperature; alternatively, 10 c.c. of the fraction are agitated with 25 c.c. of a mixture of concentrated sulphuric acid (D 1·84, 2 parts) and fuming sulphuric acid (20% oleum, 1 part) in a stoppered, graduated cylinder and the volume of undissolved paraffins is read off. H. W.

Estimation of Xylene in Solvent Naphtha. PERCY E. SPIELMANN and F. B. JONES (*J. Soc. Chem. Ind.*, 1917, **36**, 489—490).—This estimation is complicated by the fact that the xylene itself consists of three isomerides differing in b. p. and sp. gr., and that it exists as such in a complex mixture of cumene, trimethylbenzenes, and other substances which boil gradually up to 170° and over. The following procedure is recommended. Solvent naphtha (100 c.c.—or 200 c.c. if necessary for Colman's analysis) is distilled over a Young 12-pear head at the usual rate of 1 drop per second. The fractions up to 138° and from 138—170° (all temperatures being corrected) are collected in separate cylinders and measured. The benzene, toluene, and xylene in the first fractions (up to 138°) are estimated by Colman's methods for examining toluenes and solvent naphtha. The xylene in the 138—170° fraction is evaluated by determining the boiling point in a constant boiling-point apparatus, such as that due to Northall-Laurie (A., 1915, ii, 704) and reference to a graph obtained by observation of the b. p. of known mixtures of xylene and residue, b. p. 143—170°. The accuracy of the boiling-point curve may be taken as ±1·5% when the xylene content of the fraction is above 50%.

For the estimation of paraffin, 100 c.c. of the sample is distilled over a Young 12-pear head at the rate of 1 drop per second, the portion distilling between 138° and 143° (corr.) being collected separately. Ten to 20 c.c. of this fraction are vigorously shaken for about forty minutes with two and a-half times the volume of weak oleum made by mixing one volume of 22% oleum with two volumes of 95% sulphuric acid. The absorption of the aromatic hydrocarbons is effected in a 100 c.c. flask, the neck of which is graduated into 10 c.c. and subdivided into tenths of a c.c. from the volume mark upwards. After sufficient shaking, the level of the liquid is driven up into the graduated neck by the addition of a further quantity of 95% sulphuric acid. After being allowed to remain, preferably overnight, the paraffin layer is found to be sharply separated. H. W.

Stannous Chloride Reduction Method for Estimating Nitrotoluenes. E. DE W. S. COLVER and E. B. R. PRIDEAUX (*J. Soc. Chem. Ind.*, 1917, **36**, 480—483).—The authors have investigated the applicability of the methods of Knecht and Hibbert and of Altmann (A., 1901, ii, 475; reduction by stannous chloride and estimation of unused stannous salt by titration with iodine in alkaline tartrate solution) to the estimation of nitrotoluenes. With the latter method, it is essential to effect the reduction at 100°. The following method is, however, more convenient. The sample is placed in a 100 c.c. flask together with stannous chloride solution (2—2·5*N*, 20 c.c.) and concentrated hydrochloric acid (about 3 c.c.). The flask is then placed in boiling water and shaken, a blank experiment being performed at the same time. After being cooled and made up to 100 c.c., the blank and sample are diluted with water and titrated with iodine at the rate of about 2 drops per second. It is preferable to take the mean of several titrations. It is important to add the iodine at about the same rate to sample and blank, since it is found that in both cases the iodine required was less for a slow titration than for a quick one. If the iodine is added in a continuous stream to the pure stannous solution, the results of the acid titration agree most closely with those of the alkaline tartrate titration. The method has been applied to mono-, di-, and tri-nitrotoluenes, but the results are uniformly somewhat low, owing to a cause which has not yet been elucidated. The primary object of the investigation, however, was to find whether sufficiently constant numbers could be obtained to allow a calculation of the percentage composition of binary mixtures, and direct experiment shows that this can be accomplished with a very considerable degree of accuracy.

H. W.

Wet Combustion in the Nitrosite Combustion Method for the Direct Estimation of Caoutchouc. L. G. Wesson and E. S. Knorr (*J. Ind. Eng. Chem.*, 1917, **9**, 139—140. Compare A., 1913, ii, 631; 1914, ii, 593).—The method previousy described for the estimation of caoutchouc is simplified by a wet combustion of the nitrosite. The procedure is as follows. Half a gram of the finely divided sample is extracted for three hours with acetone and half an hour with chloroform, and the extracted sample is allowed to dissolve in or thoroughly absorb chloroform, and treated with nitrous acid until the green colour is permanent for fifteen minutes. After keeping overnight the chloroform is decanted through a dry Gooch crucible into the combustion flask; the chloroform is removed from both residue and filtrate by heating on a water-bath in a current of dry air. The residue is then extracted repeatedly with dry ethyl acetate and the liquid decanted through the Gooch crucible into the combustion flask until the filtered extract is colourless. After evaporation of the ethyl acetate the residue in the flask is heated on a water-bath for fifteen minutes and freed from solvent by adding 15 c.c. of water containing 1 drop of hydrochloric acid and rapidly evaporating once more to dryness in a calcium chloride bath in a current of air. The dry residue remaining in the flask is then burnt by means of sulphuric acid and potassium dichromate, collecting the products in a series of U-tubes containing calcium chloride and soda-lime. The weight of carbon dioxide obtained multiplied by the factor $(136 \times 200)/440$ gives the percentage of $C_{10}H_{16}$ in the sample.

G. F. M.

Detection and Estimation of Small Amounts of Methyl Alcohol. Elias Elvove (*J. Ind. Eng. Chem.*, 1917, **9**, 295—297).—The colorimetric estimation of methyl alcohol by Simmonds's application (A., 1912, ii, 208) of Denigès's qualitative test is rendered much more sensitive by reducing the proportion of ethyl alcohol present from 10 to 0·5%, when as little as 0·1 mg. of methyl alcohol in 5 c.c. showed a coloration after forty minutes, after treatment with 2·5 c.c. of 2% permanganate and 0·2 c.c. of concentrated sulphuric acid, decolorisation of the excess permanganate after three minutes with 0·7 c.c. of 10% oxalic acid, further acidification with 1 c.c. of concentrated sulphuric acid, and the addition when cold of 5 c.c. of Schiff's reagent. The correct preparation of the Schiff's reagent is of importance, and the following procedure is recommended. 0·2 Gram of finely powdered magenta is dissolved in 120 c.c. of hot water; 2 grams of anhydrous sodium sulphite dissolved in 20 c.c. of water are added to the cold magenta solution, followed by 2·0 c.c. of hydrochloric acid (D 1·19) and water to make 200 c.c. After keeping for an hour, the reagent is ready for use. It should be made up fresh every week.

G. F. M.

Modification of Fehling's Method of Sugar Estimation. Emil Lenk (*Deutsch. med. Woch.*, 1917, **43**, 43—44).—One mg.

of magnesium sulphate added to each c.c. of the copper sulphate solution ensures rapid sedimentation of the colloidal cuprous oxide. Calcium salts are harmful in this respect. For the estimation in urine containing less than 1 per cent. of dextrose, it is necessary to remove certain colloids by shaking for half a minute with a little blood charcoal and filtering once or twice through the same filter. On adding the urine drop by drop to boiling Fehling's solution containing magnesium, the cuprous oxide suddenly cakes together and the next drop makes the solution perfectly clear; this point corresponds with the disappearance of copper from the solution, and is therefore the true end-point. G. B.

Estimation of Sugar in Urine. L. VANINO and F. BERTELE (*Arch. Pharm.*, 1917, **255**, 134—139).—The authors have revived an almost forgotten method of the French physician, Duhomme (1874), and find it suitable for clinical purposes. Two c.c. of Fehling's solution are diluted with an equal volume of water in a series of tubes, and successive quantities of urine are counted by drops into the boiling reagent. The number of drops (x) necessary for reduction is then found by inspection. The apparatus is also tested in order to find how many drops go to make 1 c.c. (y; should be about 20—25). As 2 c.c. of Fehling's solution are reduced by 1 c.c. of 1% dextrose, y/x gives the percentage of sugar in the urine. J. C. W.

Influence of Amino-acids and of *l*-Glutimic Acid in the Estimation of Raffinose and Sucrose in Molasses by the Inversion Method. VL. STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1916, **41**, 154—160).—The presence of glutamic or *l*-glutimic acid diminishes the amount of sucrose found in all cases in which the ordinary methods of estimation are employed, only acid polarisation and the Clerget–Herzfeld formula giving accurate results.

Aspartic acid increases the amount of sucrose given by ordinary direct polarisation or by inversion and polarisation. Acid polarisation gives correct results if the Clerget–Herzfeld formula is used, but the raffinose formula gives low numbers.

In presence of aspartic or glutamic acid a positive amount, and in presence of *l*-glutimic acid a negative amount, of raffinose is indicated when this sugar is absent; the errors thus incurred are halved when acid polarisation is used.

With pure beet molasses it is well to discard the raffinose formula entirely and to determine the sugar content by the acid polarisation method and application of the Clerget–Herzfeld formula.

No method is known by which raffinose may be estimated in presence of amino-acids. T. H. P.

Direct Method for the Estimation of Starch. TH. VON FELLENBERG (*Mitt. Lebensmittelunters. Hyg.*, 1916, **7**, 369—383; from *Chem. Zentr.*, 1917, i, 450—451).—The method depends on the solubility of starch in calcium chloride solution, its precipitation by iodine, and the decomposition of the precipitate by alcohol. From 0·3 to 1·0 gram of the finely-divided, fat-free substance under examination is moistened with water and mixed with 20 c.c. of 50% calcium chloride solution; the mixture is heated in a boiling water-bath for thirty minutes, then boiled for five minutes, cooled, diluted to 100 c.c., and filtered through cotton-wool and then through asbestos. If the filtrate is not perfectly clear, it must be submitted to centrifugal action. Fifty c.c. of the filtrate are now treated with *N*/50-iodine solution until a flocculent precipitate is obtained, but a large excess of iodine is to be avoided. After about twenty-four hours a quantity of asbestos is added, the precipitate and asbestos are collected in a Gooch crucible containing a layer of asbestos, and the contents of the crucible are washed four times with 5% calcium chloride solution containing a few drops of iodine solution. The precipitate is then washed with 60% alcohol (this is allowed to act on the precipitate for five minutes), then with 85% alcohol, and finally with 100 c.c. of 90% alcohol. If the contents of the crucible are not now colourless, a quantity of hot alcohol is added. After further washing with cold 95% alcohol, 5% calcium chloride solution, and dry ether, the crucible and its contents are dried, weighed, ignited, and reweighed. The loss in weight gives the quantity of starch present.

W. P. S.

Detection and Estimation of Formic Acid in Meat Extract. Ernst Waser (*Zeitsch. physiol. Chem.*, 1917, **99**, 67—85).—For the detection of formic acid, the meat extract is subjected to steam distillation and the distillate, after reduction with magnesium and hydrochloric acid, tested for formaldehyde. The quantitative estimation is performed with 10—20 grams of the extract, which is mixed with 100 c.c. of water and 30 to 60 c.c. of 6% phosphoric acid and distilled with steam; about 1500 c.c. of distillate are collected and the amount of formic acid present estimated by Fincke's method (A., 1913, ii, 636).

Meat extracts prepared from fresh meat contain about 0·5% of formic acid calculated on the dry extract. Formic acid is present in fresh meat, and increases in amount during putrefaction. Extracts prepared from putrescent meat may contain more than 1% of formic acid.

Hehner's test for formaldehyde in milk succeeds best when the concentration of formaldehyde lies between 1:300 and 1:20,000.

H. W. B.

New Qualitative Test and Colorimetric Method for the Estimation of Vanillin. Clarence Estes (*J. Ind. Eng. Chem.*, 1917, **9**, 142—144).—Aqueous solutions of vanillin give a violet to violet-red coloration with an acid mercuric nitrate reagent after warming in boiling water for five minutes. The reagent is prepared by dissolving mercury in twice its weight of nitric acid (D 1·42) and diluting with twenty-five times the weight of water. It appears to be specific for vanillin, and can be utilised for the colorimetric estimation of this substance. In this case 5 c.c. of standard 1% aqueous vanillin solution are treated with 0·5 c.c. of the reagent, placed in boiling water for ten minutes for the development of the maximum coloration, and, after cooling, diluted to 50 c.c. with water. The unknown solution is treated in exactly the same way, unless it is a vanilla extract, in which case, since the mercuric nitrate causes the precipitation of resins and colouring matter, an excess must be used, namely, 1·5 c.c., with an alcoholic extract, or 1 c.c. with an aqueous extract, and after the development of the colour the solution is made up to 50 c.c., filtered, and compared with the standard. G. F. M.

The Possibility of Titrating Mono-substituted Amino-groups of Amino-acids and Formaldehyde. A. CLEMENTI (*Arch. ital. de biol.*, 1915, published 1916, **64**, 332—340; from *Physiol. Abstr.*, 1917, **2**, 102).—Imino-groups, for example, that of sarcosine, react in Sörensen's formaldehyde titration according to the equation $2NHRR' + CH_2O = CH_2(NRR')_2 + H_2O$. G. B.

Method for the Identification of Phenylalanine-Carbamido-acid in the presence of Urea and Amino-acid. ALICE ROHDE (*Proc. Amer. Soc. Biol. Chem.*, 1916, xxvii—xxviii; *J. Biol. Chem.*, 1917, **29**).—The urea is first decomposed by urease. After extraction of the urea-free material with ethyl acetate, the aqueous residues left on distillation with steam are analysed for traces of carbamido-acid by the gasometric method for the estimation of amino-nitrogen. Approximately quantitative results are obtained by this method when applied to urine containing known amounts of phenylalanine–carbamido-acid [α-carbamido-β-phenylpropionic acid]. H. W. B.

Detection of Cryogenine in Urine. L. GRIMBERT (*J. Pharm. Chim.*, 1917, [vii], 305—306).—Cryogenine (*m*-benzamidosemicarbazide), when rendered ammoniacal and exposed to air for twenty-four hours, is oxidised gradually and the solution becomes deep yellow in colour; the yellow colour is destroyed by the addition of sulphuric acid. If the acid solution is now shaken with ether, the ethereal solution separated and shaken with ammonia, the latter is coloured yellow. The substance may be detected in urine by rendering the latter alkaline, adding basic lead acetate, filtering the mixture, treating the filtrate with sulphuric acid, separating the lead sulphate, and then shaking the acid solution with ether. The ethereal layer is drawn off and shaken with ammonia; the alkaline aqueous layer is coloured more or less yellow, according to the quantity of cryogenine present. Oxidation of cryogenine evidently takes place in the body after administration. W. P. S.

The Estimation of Antipyrine. J. BOUGAULT (*J. Pharm. Chim.*, 1917, [vii], **15**, 337—339. Compare François, this vol., ii, 226).—The author has slightly modified his original method for the estimation of antipyrine by its conversion into iodoantipyrine (compare A., 1900, i, 312). W. G.

Sodium Perchlorate as a General Reagent in Microchemistry. G. DENIGÈS (*Bull. Soc. Pharm. Bordeaux*, 1917, **5**; from *J. Pharm. Chim.*, 1917, [vii], **15**, 322—323).—Crystals, which in some cases are characteristic, are obtained when sodium perchlorate is added to alkaloid salts in dilute solution. For instance, a 0·2% brucine solution yields hexagonal plates or rhombic octahedra, whilst a 0·1% strychnine solution gives long, needle-shaped crystals. Cocaine (A., 1915, ii, 74), berberine, narceine, cotarnine, and papaverine also yield crystals when treated with sodium perchlorate, whilst veratrine and narcotine give amorphous precipitates. W. P. S.

Microchemical Precipitation of Alkaloids with Zinc Chloride-Iodine Solution. O. TUNMANN (*Apoth. Zeit.*, 1917, **62**, 76—78; from *Chem. Zentr.*, 1917, i, 701—702).—The results were obtained with more or less impure alkaloid residues, such as are prepared by the Stas-Otto method. The reagent does not yield crystalline products with arecoline, brucine, cocaine, quinine, cinchonine, coniine, colchicine, narceine, nicotine, eserine, or veratrine. On the other hand, it is well adapted for the identification of strychnine, sparteine, the opium alkaloids, morphine, papaverine, cryptopine, and codeine, as well as atropine and hyoscyamine. With atropine, brown or dark red to blackish-red crystals, mostly rhombs, are immediately produced, which, at the commencement of the reaction, vary greatly in size. All the crystals shine but little between crossed Nicols, and do not exhibit pleochroism. The crystal crosses, consisting of four rhombs, are particularly characteristic. The limit of sensitiveness is 10—20 μg. The iodide crystals of hyoscyamine shine feebly in polarised light; they are very small (4—8 μ), almost black, and without pleochroism. The platelets have generally a far less regular circumference than the atropine crystals. Limit of sensitiveness, 10 μg. Zinc chloride-iodine yields crystals even with very impure morphine preparations; initially, fine, pale brown needles are formed, which after ten to twenty minutes unite to sheaves, and are then transformed into prismatic crystals with direct extinction. The latter are brown, the larger ones being nearly black; they do not exhibit pleochroism and scarcely shine between crossed Nicols. Limit of sensitiveness, 5 μg.

Papaverine and cryptopine give long, dull red, yellowish-red, or greenish-red crystals from 2—3 μ diameter which have direct extinction, show red to blue polarisation colours, and exhibit pleochroism. The latter phenomenon yields an excellent method of differentiating between the three opium alkaloids considered here. Limit of sensitiveness, about 10 μg. In addition to the crystals described above, deep red drops are also formed which, after some hours, pass into deep red aggregates; this points to the presence of a second alkaloid (? cryptopine) in papaverine.

Codeine behaves very differently. A powdery precipitate is first obtained, which when warmed deposits larger and smaller particles, from which very slender, generally curved, pale brown crystals grow. The limit of sensitiveness is about 40 μg. Excess of the reagent is to be avoided. Sparteine is preferably converted into the sulphate, and this gives with the reagent fine, yellowish-red crystal threads, which form sheaves and brushes at their ends. When warmed, coarser prismatic crystals appear after about thirty minutes, and in addition, when further heated, yellow aggregates are occasionally obtained. All the crystals shine strongly in polarised light, have extinction parallel to the long axis, and show very marked pleochroism. When warmed with zinc chloride–iodine, strychnine gives brownish-red or blackish-red spheres or aggregates which attain a diameter of 50 μ, and lie separately or are grouped in chains. They glow red between crossed Nicols, but do not exhibit pleochroism. Limit of sensitiveness, 15 μg.

Unless specific mention to the contrary is made, the above data refer to the crystals which are produced after one to two hours' action. H. W.

Detection of Atropine and Related Mydriatic Alkaloids. R. Eder (*Schweiz. Apoth. Zeit.*, **54**, 501—504, 517—520, 534—537, 544—548, 560—563, 609—612, 621—624, 657—661, 669—670, 685—687, 717—719; from *Chem. Zentr.*, 1917, i, 448—500).—The methods employed in the detection of atropine and related mydriatic alkaloids are critically reviewed, and two new reagents for the detection and differentiation of the more important of these bases are described.

Bromine water and bromine–potassium bromide are recommended as reagents for the microchemical detection of the *Solanaceae* bases. A drop of the solution of the alkaloid in $N/2$-sulphuric acid is brought on to an object-glass, and a drop of the reagent is added; after a short time, with small magnification, a fine turbidity appears, followed more or less rapidly by the formation of minute crystals, which present the appearance of fine, pale yellow needles. The crystals rapidly increase and sink to the bottom of the liquid, which gradually becomes clear. In the inner portions, individual needles frequently grow to stout, yellow rods; at the edge of the drop, on the other hand, the needles speedily begin to disappear, whilst the solution becomes colourless. The crystals also disappear more or less rapidly from the inner portions, and the solution becomes colourless as the bromine evaporates. The shape of the crystals is best studied with a 180—250 times magnification, and the solution should be protected with a cover-glass, thus rendering the crystals more stable. They are fully described and figured in the original. The reaction of atropine towards bromine water has the advantage over other atropine reactions that it can be repeated as often as desired with one and the same specimen. When the solution has become clear and colourless, the characteristic precipitate can be again obtained by renewed application of bromine water. The reaction is distinctly obtained at dilution of 1 in 3000. The macrochemical behaviour of atropine in $N/2$-sulphuric acid solution towards bromine–potassium bromide [Br (1 gram), KBr (2 grams), water

(20 grams)] is similar to its action on bromine water, but the reaction is considerably more sensitive.

Hyoscyamine reacts with bromine water in much the same manner as atropine. The yellow, cloudy precipitate rapidly becomes crystalline, and disappears as the bromine evaporates. The highly magnified crystals, however, have a very variable character. For this reason, bromine water is a less suitable reagent for the detection of the alkaloid than bromine–potassium bromide. The limit of sensitiveness of the latter is reached at a dilution of about 1 in 5000. By means of the reaction, atropine can be detected in the presence of hyoscyamine in a mixture of the alkaloids.

The macrochemical behaviour of homatropine and scopolamine towards bromine water and bromine–potassium bromide exactly resembles that of atropine. The yellow precipitate obtained from scopolamine with bromine water appears under the microscope to consist exclusively of amorphous drops, crystallisation only occurring infrequently and at isolated points. Similar results are observed with bromine–potassium bromide. The precipitate of homatropine with bromine water is at first amorphous, but rapidly becomes crystalline, whilst that with bromine–potassium bromide closely resembles the precipitate with atropine.

With the exception of caffeine, the remaining alkaloids, which yield yellow or otherwise coloured precipitates with bromine water or bromine–potassium bromide, give only amorphous deposits. The crystalline compound from caffeine may be useful in the detection of the latter. Iodine–potassium iodide gives reddish-brown, crystalline precipitates with atropine, hyoscyamine, and homatropine, which are less characteristic than the bromine–potassium bromide compounds. With scopolamine, as with most other alkaloids, the precipitates are amorphous. Labile bromine additive compounds which readily lose bromine are probably formed from the two reagents described above and the mydriatic alkaloids.

With regard to the detection of atropine and related alkaloids, the author draws the following conclusions. There is no single reaction on which dependence can be placed for the detection of these substances. Of the many reactions which have been previously proposed, only a few are suited to the practical detection of the bases. The following are to be recommended: physiological examination, Vitali's reaction, behaviour towards concentrated sulphuric acid in the cold (no coloration) and in the warm (odour after addition of water). Of colour reactions, with the exception of the negative tests with Froehde's and Erdmann's reagent, only Wasicky's reaction with dimethylaminobenzaldehyde and, possibly, Arnold's reaction need to be considered. Among microchemical methods and reactions, micro-sublimation, the iodine–atropine salt, and, particularly, the reactions with bromine water and bromine–potassium bromide, give good results. In the presence of other alkaloids which give amorphous precipitates with the bromine reagents, a separation is necessary which can frequently be effected by micro-sublimation. H. W.

Distillation of Nicotine with Steam. Hans Brezina (*Fachl. Mitt. österr. Tabakregie*, 1916, 3 pp.; from *Chem. Zentr.*, 1917, i, 700—701).—With the object of obtaining a greater concentration of nicotine in the vapour without employing the salting-out method, the author passes a current of steam through a series of flasks containing a solution of nicotine; each flask is heated at 102°. In this manner, the steam can be caused to contain as much as 4% of nicotine, and considerable economy is effected in the time of distillation. Complete removal of nicotine from its solutions cannot be effected by this means, but the method yields the maximum effect in a shortened time. H. W.

Estimation of Theobromine. Léon Débourdeaux (*J. Pharm. Chim.*, 1917, [vii], **15**, 306—311).—The theobromine obtained from cocoa by Maupy's method (A., 1897, ii, 531) contains from 6 to 12% of impurity, and the author suggests the following alterations in the process with the object of separating the alkaloid in a pure state. One hundred grams of the cocoa are mixed with 40 grams of water and boiled for two hours with a mixture of 60 grams of phenol and 340 grams of chloroform; the liquid portion is then separated and the residue extracted twice with chloroform containing phenol, the mixture being boiled for one hour in each extraction. After filtration, the extracts are distilled to remove the chloroform, the residue is mixed with 900 grams of ether, and, after about eighteen hours, the precipitated theobromine is collected, washed with ether, then dissolved in warm dilute sulphuric acid (20 grams of sulphuric acid and 180 grams of water), and the solution is filtered into a flask containing 250 c.c. of ammonia; the ammoniacal solution is treated with 2 grams of silver nitrate, then evaporated until all free ammonia has been expelled, diluted to 500 c.c., and the precipitated silver–theobromine compound collected after twenty-four hours. The precipitate is washed with 250 c.c. of water, then mixed with water, decomposed with hydrogen sulphide, 600 grams of amyl alcohol are added to the mixture, and the whole is distilled until 200 c.c. of distillate (water plus amyl alcohol) have been collected. The residual amyl alcohol solution is filtered, kept at 15° for thirty-six hours, the crystallised theobromine then collected, washed with ether, dried at 100°, and weighed. The weight of the amyl alcohol filtered from the crystals should be noted; 1000 grams of amyl alcohol at 15° dissolve 0·200 gram of theobromine, and a corresponding correction is applied to the weight of theobromine obtained. W. P. S.

General and Physical Chemistry.

Molecular Refractivities of Certain Elements and Simple Compounds. GERVAISE LE BAS (*Chem. News*, 1917, **115**, 277—278).—A discussion of the refractivities of simple oxygen and nitrogen compounds with reference to the augmentation supposed to be due to unsaturation. H. M. D.

Measurements in the Short-waved Portion of the Arc Spectrum of Vanadium. WILHELM LUDWIG (*Zeitsch. wiss. Photochem.*, 1917, **16**, 157—185).—A detailed record of wave-lengths of lines in the arc spectrum of vanadium from λ 2207 to λ 4646. The relative intensities of the lines are indicated and the numbers compared with those given by previous observers. H. M. D.

Quantitative Light-filter for the Ultra-violet Part of the Spectrum. N. P. PESKOV (*J. Physical Chem.*, 1917, **21**, 382—401).—It has been found that a gaseous mixture of chlorine and bromine may be advantageously used as a light-filter for the region $\lambda=500$ to $220\,\mu\mu$. By a modification of Henri's photographic method, the author has determined the absorption-coefficients of gaseous chlorine and bromine for forty-three lines of the ultra-violet spectrum emitted by an arc between iron and copper electrodes. The absorption of mixtures of the two gases satisfies the requirements of Beer's law. The distribution of radiant energy in the light transmitted by various mixtures has been determined. H. M. D.

Colour and Chemical Constitution. Quantitative Study of the Phthaleins and of other Fuchsone Derivatives. JAMES MOIR (*Roy. Soc. South Africa*, 1917).—Wave-length measurements of the absorption bands have been made for a series of about fifty derivatives of phenolphthalein and fluorescein in alkaline solution, and also when dissolved in concentrated sulphuric acid. The results lead to the conclusion that the change of colour which accompanies substitution is mainly due to the change in volume which is caused by the entry of the substituent element or group, the effect being more pronounced when the substitution occurs in the vicinity of the quinonoid linking.

In alkaline solution, the absorption bands of the derivatives of phenolphthalein are all displaced towards the region of greater wave-lengths as compared with the band of the parent substance. The magnitude of the displacement increases with the volume of the substituting element or group. Substitution in the meta-position produces an effect which is usually about twice as great as that produced by the same substitution in the ortho-position. Substitution in the phthalic ring has comparatively little influence on the colour. Derivatives of fluorescein show the same relations as phenolphthalein derivatives, but it is to be noted that the oxo-linking in fluorescein is exceptional in its influence in that the band is displaced towards the region of shorter wave-lengths as compared with the phenolphthalein band.

In concentrated sulphuric acid solution, the colour is about five times as intense as that of the same substance in alkaline solution, and in all cases there is a difference in colour, the wave-length being shorter in the sulphuric acid solution. The wave-length data show the existence of a connexion between the wave-lengths of the bands for a particular substance in alkaline solution on the one hand and in sulphuric acid solution on the other.

If λ is the wave-length of the absorption band in alkaline solution and λ_1 the wave-length in sulphuric acid, then the relation between λ and λ_1 may be expressed by the equation $1/\lambda_1=3/2\lambda-c$, where c is a constant. The constant in the equation is supposed to represent the effect produced by combination of the substance with sulphuric acid, and it is suggested that the influence in question may be due to the formation of a ring structure in which the two phenolic hydroxyls are joined up by the sulphuric acid. The phenol rings thus form a part of the complex ring structure and occupy the same relative position as in fluorescein. H. M. D.

Absorption of X-rays. Tycho E:son Aurén (*Phil. Mag.*, 1917, [vi], **33**, 471—487).—From a review of existing determinations, it appears that the ratio of the absorption-coefficients of two materials must be independent of the wave-length of the *X*-rays outside of the range of wave-length wherein selective absorption occurs and for rays of not too great wave-length. A new method, based on this, is described for accurately determining the absorption-coefficient of any element relative to that of water, for the most part by experiments on aqueous solutions of the salts of the element in question. The absorption of the solution of known concentration, considered as additively determined by the absorption of its constituent atoms, is accurately balanced by varying the thickness of the solution traversed against that of a standard water cell. Two ionisation chambers opposed to one another are used, and the current adjusted to zero by varying the thickness of the solution layer. The relative molecular absorption-coefficient, in terms of that of water as unity, is independent of the concentration of the solution, and has been determined for some forty-five substances, and from these the relative atomic coefficients of the constituent elements have been deduced. Similar determinations have also been made with some metals and with organic compounds. For example, from the cases of water, sodium chloride, and sodium chlorate, the values, for hydrogen 0·05, for oxygen 0·9, are found, the value for water being unity. The value so found for cobalt, 53·9, is intermediate between those for iron and nickel, 45·5 and 59·4 respectively, in good agreement with existing knowledge as to the position of this element in the periodic table. There is some slight indication that the value for carbon in aromatic compounds is lower than in the aliphatic compounds, and also that that for ferrous iron is lower than for ferric iron, but more exact measurements are required to establish these points.

Plotting the relative atomic absorption-coefficients against the atomic numbers gives an interesting curve with several abrupt changes of slope, the absorption-coefficient increasing continuously with the atomic number, slowly from hydrogen to chromium, then much more rapidly, and, on the average, fairly linearly from chromium to silver, where the slope much decreases. In the region from platinum to bismuth the slope is very steep, whereas for uranium the coefficient is almost twice that of bismuth, the next lower element examined.

The values of the relative atomic absorption-coefficients of the elements determined are set forth in the following table:

Atomic number	1	6	7	8	11	12	13	14	15
Element ...	H	C	N	O	Na	Mg	Al	Si	P
Rel. at. abs. coeff.	0·05	0·46	0·63	0·9	1·9	3·5	3·4	4·1	5·68

Atomic number	16	17	19	20	24	25	26	27	28
Element ...	S	Cl	K	Ca	Cr	Mn	Fe	Co	Ni
Rel. at. abs. coeff.	7·78	9·5	11·1	14·4	24·1	41·4	45·5	53·9	59·4

Atomic number	29	30	33	35	38	42	47	48	50
Element ...	Cu	Zn	As	Br	Sr	Mo	Ag	Cd	Sn
Rel. at. abs. coeff.	65·1	75·4	128	154	173	244	300	301	311

Atomic number	52	56	58	74	78	80	82	83	92
Element ...	I	Ba	Ce	W	Pt	Hg	Pb	Bi	U
Rel. at. abs. coeff.	315	334	327	308	529	547	569	677	1123

The X-rays used were from a bulb with tungsten anticathode, filtered through an aluminium screen 1·25 mm. thick. For the reasons referred to at the commencement, the rays, though not homogeneous, probably behaved in the same way as homogeneous X-rays, although the value for tungsten is doubtless vitiated by selective absorption. An increase in absorption occurs apparently with solutions in the colloidal state. F. S.

Initial Charged Condition of the Active Deposits of Radium, Thorium, and Actinium. G. H. Henderson (*Trans. Roy. Soc. Canada*, 1917, [iii], **10**, 151—167).—The requirements of the testing vessel to enable the percentage to be determined of the atoms recoiling from the emanations which are neutral or charged are discussed, and an apparatus for this purpose described. In dry air all the residual atoms are probably positively charged, whereas in pure ether vapour, and probably in pure water vapour, all of them are uncharged. In a mixture of air and vapour, the proportion of neutral and positively charged atoms depends on the proportion of the mixture. This seems to be general, hydrogen, oxygen, carbon dioxide, etc., giving all positive, ether, water, and ethyl bromide vapours giving all neutral recoiling atoms. Though differences exist in the behaviour of the three emanations, it is probable that all three types of recoiling atom are similarly affected by the surrounding gas and the electric field. The charged or neutral condition of the recoiling atom is not a consequence of what occurs at the disintegration, but must be ascribed to the gas molecules encountered during its recoil. Collision with certain gas molecules ionises it as well as the molecule struck, whereas with others, whatever its state before collision, after collision it escapes always uncharged. The character of the charge carried at the instant of its formation from the emanation atom does not affect the problem, and is not discussed. F. S.

The Motion of Ions and Electrons through Gases. E. M. WELLISCH (*Phil. Mag.*, 1917, [vi], **34**, 33—66).—In previous experiments on the mobility of ions in air at varying pressures, it has been found that the increase in the value of the product of the mobility and the pressure for negative ions at low pressures is due to the fact that electrons and ions act as carriers, and that the proportion of the current carried by the electrons increases as the pressure is reduced. When the ions alone are considered, the product of mobility and gas pressure remains constant. Further experiments on the mobility of the negative ions in hydrogen and carbon dioxide have given the same result in that the mobility of the negative ions varies inversely as the pressure of the gas.

The proportion of electrons to ions in a gas at a given pressure is known to depend very largely on the nature of the gas, and it appears that gases and vapours which contain electronegative elements are favourable to the formation of negative ions. The vapour of light petroleum contains a very small proportion of negative ions, but a trace of an active substance is sufficient to produce a large number of ionic carriers, a result which agrees with previous experiments on inert gases.

The investigation of the motion of the electrons through carbon dioxide has given results which suggest that the electron may traverse a considerable distance with accelerated motion before its final velocity is acquired. There was no evidence of any change in the nature of either the positive or the negative ion when the pressure of the gases experimented on was reduced.

The results are discussed in reference to various problems connected with the ionisation of gases. H. M. D.

The Discharge Potentials of Ions on Heated Electrodes. I. JNANENDRA CHANDRA GHOSH (*J. Physical Chem.*, 1917, **21**, 426—432).—Measurements of the discharge potential were made for the chlorine, bromine, sulphate, and nitrate ions at 30° and

96°. The temperature of the platinum wire anode was varied by passing a suitable current through a circuit, of which the anode formed part. The results obtained indicate that the phenomenon of overvoltage has disappeared at the higher temperature, and further, that the discharge potentials for the chlorine and bromine ions at 96° are less than their respective normal electrode potentials. H. M. D.

Photoelectric Ionisation of Solutions. MAX VOLMER (*Zeitsch. wiss. Photochem.*, 1917, **16**, 186—189).—Under the influence of ultra-violet rays of very short wave-length, solutions of anthracene in hexane show a very large increase in their electrical conductivity. In the apparatus used by the author for the investigation of this effect, the conducting power of the illuminated solution was one to two thousand times as great as that of the same solution in the dark. The same effect has been found with solutions of methylanthracene, phenanthrene, chrysene, stilbene, α- and β-naphthol, diphenylamine, α-naphthylamine, quinizarine, and naphthazarine. In all cases the active rays are of wave-length less than $\lambda = 225\ \mu\mu$. H. M. D.

Measurement of Oxidation Potentials at Mercury Electrodes. II. The Chromic-Chromous Potential. GEORGE SHANNON FORBES and HERMAN WILLIAM RICHTER (*J. Amer. Chem. Soc.*, 1917, **39**, 1140—1148. Compare A., 1914, ii, 795).—Using the same method as previously adopted for measurement of the stannic–stannous potential (*loc. cit.*), the authors have determined the oxidation potential of chromic–chromous chloride. Pure violet chromic chloride was partly reduced to chromous chloride by heating in a current of hydrogen in a quartz tube at 400°. The mixture was dissolved in ice-cold $0 \cdot 1N$-hydrochloric acid. The solution thus prepared was filtered into the cell and allowed to remain over pure mercury. When all operations were carried out in either hydrogen or carbon dioxide absolutely free from oxygen, the potential rose continuously to a maximum constant value, which was reached in two days. If oxygen was present even in traces, the potential fluctuated irregularly. When the equilibrium potential had been obtained, the solution was analysed. Referred to the normal hydrogen electrode as zero, with correction for junction potentials, and at 25° $\pi = -0 \cdot 400 + 0 \cdot 065 \log Cr^{III}/Cr^{II}$. On platinum, the potentials reached a maximum about 0·16 volt lower than that on mercury, with the evolution of hydrogen. J. F. S.

Applicability of the Isohydric Principle to Decinormal Mixtures of Hydrochloric Acid and Potassium Chloride. N. EDWARD LOOMIS, J. L. ESSEX, and MERLE R. MEACHAM (*J. Amer. Chem. Soc.*, 1917, **39**, 1133—1139. Compare this vol., ii, 13). —It was previously shown (*loc. cit.*) that the potential of a $0 \cdot 1N$-potassium chloride calomel electrode is identical with that of a $0 \cdot 1N$-hydrochloric acid calomel electrode. This indicates that at the concentration $0 \cdot 1N$ these two substances are equally dissociated. In accordance with the isohydric principle it follows that if $0{\cdot}1N$-potassium chloride and hydrochloric acid are equally dissociated, these solutions may be mixed in any proportion without changing their degree of dissociation, and in such a mixture, both substances will have that degree of dissociation which they would have had had they been present alone in the same volume. With the object of testing this, the *E.M.F.* of cells of the type H_2,Pt|$0{\cdot}1N$(HCl + KCl)|Hg_2Cl_2|Hg have been measured, in which the sum of the hydrochloric acid and potassium chloride is $0{\cdot}1N$ and in which the hydrochloric acid varies between $0{\cdot}01N$ and $0{\cdot}09N$ and the potassium chloride varies between $0{\cdot}09N$ and $0{\cdot}01N$. In every case it is shown that the *E.M.F.* of the system is higher than the value calculated from the isohydric principle. This result has been explained by the conclusion that the isohydric principle does not apply rigidly, but that there is a slight increase in the dissociation of the hydrochloric acid with increasing proportions of potassium chloride. In the most extreme case, the mixture of $0{\cdot}01N$-HCl + $0{\cdot}09N$-KCl, the dissociation of the acid appears to have increased from 86% to 86·68%. The reason for this increase is not definitely indicated by the present work. J. F. S.

Inclusions in Silver Voltameter Deposits and the Electrochemical Equivalent of Silver. W. M. Bovard and G. A. Hulett (*J. Amer. Chem. Soc.*, 1917, **39**, 1077—1103. Compare A., 1916, ii, 213).—In a previous paper (*loc. cit.*) the nature and amount of the inclusions in the cathode deposit of various silver voltameters were determined. The present paper deals with an experimental comparison of the anode loss and cathode gain in silver voltameters. A special form of voltameter, based on that devised by Smith (*Nat. Phys. Lab.*, 1910, 32) has been used, and it is shown that the loss from a silver anode agrees with the cathode gain to within 7 parts per 100,000 when the weight of the cathode deposit is corrected for inclusions. This error is to be regarded as a maximum, since the process involves considerable manipulation, which would tend to make the divergence between the two quantities larger. An improved apparatus is described for measuring the amount of inclusions, and this gives an accuracy of 0·001%. The amount of inclusions in the deposit on a standard platinum cup voltameter has been found to be 6·7 parts per 100,000. Calculating from this value, it is shown that the value of the electrochemical equivalent of silver is 1·11798 and the value of the faraday is 96,496. The inclusions in deposits on silver cathodes are of the same value as those on platinum to within 1 part per 100,000, a value of 7·7 per 100,000 having been obtained. The silver deposit on a silver wire in the special form of apparatus used for the anode loss and cathode gain comparison has been found to contain very large amounts of inclusions. The explanation of this has not been discovered. The values obtained for the faraday by means of (*a*) the silver voltameter, (*b*) the iodine voltameter, and (*c*) the cadmium voltameter have been compared. The divergence is attributed to a possible error in the atomic weight of cadmium. J. F. S.

The Hydration of Ions and Metal Overvoltage. EDGAR NEWBERY (T., 1917, **111**, 470—489. Compare this vol., ii, 64).—The cathodic and anodic overvoltages of a number of metals have been investigated in sulphate, nitrate, and chloride solutions, attention being directed to the influence of time and of current density on the overvoltage. Some observations were also made on solutions containing colloidal substances.

In general, the cathodic overvoltages are less than 0·05 volt, but are much higher for iron, nickel, and cobalt. The anodic overvoltages are also low unless the metal deposition is accompanied by passivity. This was observed with iron, nickel, and thallium. The results obtained support the view that metal overvoltages are mainly due to the formation of solid solutions of hydrides, higher oxides, etc., on or in the electrodes. The cathodic solid solutions are very dilute except in the case of iron, nickel, and cobalt, and it is to this circumstance that the high overvoltages shown by these three metals are to be attributed. The presence of hydrides in these three metals has affected all previous determinations of the normal potentials of these metals, and a reinvestigation of these potential differences has shown that accurate and reproducible values can only be obtained in the absence of free hydrogen and metallic hydrides. Even in these circumstances the value of the single potential difference for the three metals in question is not quite determinate, for rapid motion of the electrode relative to the electrolyte produces an appreciable change. This phenomenon is supposed to be connected with the hydration of the corresponding ions, which are thus similar to the hydrogen and hydroxyl ions, whilst most other ions appear to be non-hydrated.

The hydrated and non-hydrated ions behave differently towards colloids, in that these are carried into the metal surface by hydrated ions only and have no influence on overvoltage and little or none on the nature of the deposited metal unless hydrated ions are involved in the electrolytic process.

Previous attempts to determine ionic hydration by the use of a reference substance are criticised adversely. H. M. D.

Electroreduction of the Nitrates of Potassium and Lithium by the Alternating Current. J. KLIATCHKO and CH. BINGGELY (*Ann. chim. anal.*, 1917, **22**, 81—84).—Various metals were used as electrodes, either fixed or rotating. Both with lithium and potassium nitrate the best reduction was obtained with electrodes of cadmium, the least reduction being obtained with copper. There was always a greater reduction with rotating than with fixed electrodes, and in all cases the electrodes became coated with a more or less thick layer of oxide, this being particularly marked for aluminium. The more dilute the solution of the electrolyte, the higher was the percentage reduction. The reduction was increased by the presence of sulphuric acid, but in these cases there was a rapid destruction of the electrode. W. G.

Magneto-chemistry of the Compounds of Chromium. I. Chromic Sulphate and Nitrate. B. CABRERA and M. MARQUINA (*Anal. Fis. Quim.*, 1917, **15**, 199—209).—An account of the determination of the magneto-chemical data of chromic nitrate, and of the violet and green chromic sulphates. A. J. W.

Dilatability of Argon and Neon. Internal Pressure in Monatomic Gases. A. Leduc (*Compt. rend.*, 1917, **164**, 1003—1005).—The coefficients of dilatability of argon and neon were found experimentally to be $3669 . 10^{-6}$ and $3664 . 10^{-6}$ respectively, from which, by calculation, their internal pressures are determined as $190 . 10^{-5}$ atmos. and $53 . 10^{-5}$ atmos., which values support the hypothesis that the internal pressures in monatomic gases are proportional to the squares of their molecular masses. W. G.

Changes in the Expansion of Alloys of Iron and Nickel under the Action of Different Thermal or Mechanical Treatments. Ch. Éd. Guillaume (*Compt. rend.*, 1917, **164**, 904—906. Compare *ibid.*, 1916, **163**, 654, 741, 966).—The alloys examined had a nickel content varying from 27·5—69·0% of nickel. The alloys were tempered, annealed in the ordinary manner or very slowly in sand, or tempered and drawn. In certain cases, after the slow annealing, the specimens were heated to a red heat and cooled in the air. With the alloys of low nickel content, all the methods of thermal and mechanical treatment resulted in an increase of the coefficient of expansion. For an intermediate nickel content, all the treatments caused a lowering of this coefficient, which was partly permanent after reheating and cooling in air. The alloys with higher nickel content, 42—69%, behaved in the same manner as invar (*loc. cit.*), but with smaller changes. W. G.

Molecular Attraction. XIV. Specific Heats of the Elements and some Energy Changes. J. E. Mills (*J. Physical Chem.*, 1917, **21**, 345—381).—The literature of the specific heats of the elements has been examined and the available data utilised in drawing up a series of tables in which the specific heats of the elements are given at various temperatures covering the range over which measurements have been made. In some cases the data for the three states of aggregation are recorded, and these are supplemented by heats of fusion and heats of vaporisation. H. M. D.

Measurement of Cryoscopic Constants at Elevated Temperatures. J. Howard Mathews (*J. Amer. Chem. Soc.*, 1917, **39**, 1125—1133).—An apparatus is described for the determination of cryoscopic constants at elevated temperatures. It consists of a freezing tube 20 cm. long and 4 cm. diameter; this is placed inside a slightly larger tube which serves as an air-jacket. The two tubes are placed inside the heating chamber, which consists of a long-necked bulb fitted with a wide side-tube at the top and a narrow side-tube at the bottom which makes connexion between the bulb and the top side-tube. A water condenser is attached to the top side-tube and to a manostat. An automatic stirrer and thermometer are placed in the freezing tube. To obtain the required temperature of the heating jacket, a liquid, preferably a hydrocarbon or mixture of hydrocarbons, is used, and the boiling point is regulated by varying the pressure. Sometimes it is found that the solvent sublimes and condenses in the neck of the tube, thus altering the composition of the solution; this is obviated in the present apparatus by means of an electrically heated platinum spiral. It is shown that this apparatus can be used for a large number of substances covering a wide range of melting points, since it is possible to secure the necessary adiabatic conditions by simply choosing a liquid of an appropriate boiling point for the mantling vapour. It is claimed that the more serious sources of error usually found in such cryoscopic measurements, in particular the errors due to imperfect adiabatic conditions and to the sublimation of the solvent, are removed. The limit of accuracy seems to be limited to the accuracy with which temperatures can be read by the thermometer, namely, 0·001° in the case of a mercury thermometer. To test the apparatus, the cryoscopic constant (K) and the latent heat of fusion (L) of several substances have been determined. The following values are given in the paper: anthracene, $K=68·99$, $L=35·70$ cal.; acetanilide, $K=69·32$, $L=42·87$ cal.; benzoic acid, $K=87·88$, $L=34·80$ cal. In the case of solutions of anthracene in cinnamic acid, the value of K decreases with increasing concentration, from which it is concluded that anthracene associates in cinnamic acid.

J. F. S.

The Nature of Chemical Affinity in the Combustion of Organic Compounds. W. M. Thornton (*Phil. Mag.*, 1917, [vi], **34**, 66—70).—By reference to the data for the aliphatic hydrocarbons, it is shown that the heat of combustion, H, is related to the molecular weight (m_1) of the hydrocarbon, and the weight (m_2) of the oxygen atoms required for its complete combustion by the equation $H^2/m_1m_2=$constant. As a matter of fact, the value of this expression falls slightly at first as the molecular weight of the hydrocarbon increases, but soon becomes constant.

This constancy is supposed to afford evidence in favour of the view that the operation of chemical affinity is governed by a law of the gravitational type. In support of this view, the author quotes the results of Bone's experiments on the distribution of oxygen between methane and hydrogen. These experiments showed that in a mixture of the composition $CH_4+O_2+H_2$ at high initial pressure, 97·1% of the oxygen reacted with methane and only 2·9% with hydrogen. The products of the masses corresponding with complete combustion are respectively 16×64 and 2×16, giving a ratio 32:1, which is very close to the experimentally observed ratio of distribution in the explosion experiments.

H. M. D.

The Volumes of the Atoms at Absolute Zero. Gervaise Le Bas (*Chem. News*, 1917, **116**, 1—2).—An attempt is made to estimate the volumes occupied by different atoms in a state of chemical combination at absolute zero. The atomic volume of combined hydrogen is 2·340, and the relative volumes of other atoms are given by the equations $C=4H$, $N=4H$, $Cl=6H$, $O_2=5H$, $>O=3H$.

The ratio of the critical volume to the volume at absolute zero is 4·11, and from the data for the aliphatic hydrocarbons the author draws the conclusion that the molecular volume at absolute zero (V_0) is connected with the molecular refractivity (M_α) by the equation $V_0/M_\alpha=3{\cdot}0$. H. M. D.

Molecular Constitution of Pure Liquids. III. P. N. Pavlov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1728—1744. Compare this vol., ii, 293).—Examination of the values of N for nineteen liquid compounds of different chemical characters over a widely reduced temperature interval shows that in most cases this magnitude varies with the temperature. Practical constancy is observed with methyl formate and stannic chloride, and the remaining compounds are divided into three groups: (1) With methyl, ethyl, and propyl alcohols, acetic acid and water, the value of N at first decreases to a minimum as the temperature rises, and afterwards gradually increases to the temperature of crystallisation; an indistinct minimum also occurs with *n*-hexane, *n*-heptane, *n*-octane, and di*iso*butyl. (2) With benzene, chloro-, bromo-, iodo-, or fluoro-benzene, *n*-pentane, di*iso*propyl, *cyclo*hexane, and methyl formate, small variations in the value of N are observed, but these are so small and irregular that independency of the temperature may be assumed; in the neighbourhood of the critical temperature N increases.

With the saturated hydrocarbons at identical reduced temperatures, the ratio of the abnormality number N to the total number of atoms in the molecule is independent of the molecular weight of the hydrocarbon, so that $N_{\text{corr.}}:n$ is a universal constant; the ratio $N:n$ is termed the atomic coefficient of abnormality. This ratio varies only slightly with the temperature. Structural isomerism has but little influence on the molecular constitution of liquids as expressed by the abnormality number.

The numerical magnitude of the influence of ring-closure on the value of N in the case of *cyclo*hexane is $-0{\cdot}06766$; thus, the closure of the ring increases the association or diminishes the dissociation of a liquid, whereas introduction of a new carbon or hydrogen atom into the molecule decreases the association or increases the dissociation. The coefficient of abnormality of the double linking, calculated from the value for ethylene, is $+0{\cdot}06525$, such linking diminishing the association or increasing the dissociation. The above values refer in all cases to the reduced temperature 0·9829.

If the benzene molecule is regarded as a closed ring, its abnormality number is in agreement with the presence of three (actually 2·98) double linkings in the molecule.

The atomic abnormality-coefficient for carbonyl oxygen is 0·15068 with acetaldehyde and 0·14199 with acetone, the mean being 0·14634. For hydroxylic oxygen, however, the atomic coefficient of abnormality, even for one and the same reduced temperature, is not a constant magnitude, but diminishes as the number of atoms in the molecule increases. At the reduced temperature 0·6054, the value of this coefficient is 7·774, 6·152, and 3·950 for the oxygen in methyl, ethyl, and propyl alcohols respectively. The value for the chlorine atom is virtually constant, being 0·2416, 0·2316, 0·2229, 0·2307, 0·2337, and 0·2292 for methyl, ethyl, and propyl chlorides, chloroform, carbon tetrachloride, and chlorine itself at the reduced temperature 0·6054. For the nitrogen atom at the same reduced temperature the value is 0·1696, 0·18478, 0·17810, 0·15820, 0·28083, 0·27718, and 0·26979 with nitrogen itself, ammonia, ethylamine, propylamine, aceto-, propio-, and butyro-nitriles respectively.

The abnormality number of a liquid is a constant number and is unchanged by chemical reaction, so that in chemical changes between liquids the number of the reacting molecules is equal to the number of the resultant molecules if corresponding temperatures are employed in all cases. Further, if the molar volumes of the four liquids taking part in the reaction, $A_1+A_2=A_3+A_4$, are v_1, v_2, v_3, and v_4 respectively, and their abnormality numbers at corresponding temperatures N_1, N_2, N_3, and N_4, it is readily shown that $N_1+N_2=N_3+N_4$ if $v_1+v_2=v_3+v_4$, that is, the molar volumes of the liquid compounds taking part in a chemical reaction are not changed in magnitude if the initial system consists of the same number of molecules as the final system. T. H. P.

Measurement of the Absolute Viscosity of very Viscous Media. S. E. Sheppard (*J. Ind. Eng. Chem.*, 1917, **9**, 523—527).—The application of Stokes's law connecting the rate of fall of a spherical substance with the viscosity of the medium is discussed in reference to very viscous media, and particularly with regard to the influence of the boundary walls of the containing cylinder. Stokes's law assumes the medium to be infinite in extent compared with the diameter of the sphere, that is, T is constant when $R'/R=r=\infty$, where T is the time of fall through length S and R' and R are the respective radii of the cylinder and the sphere. An empirical formula is worked out which corrects for the influence of the boundary wall and is valid over a wide range, namely, $T=T_\infty+C/(r-1)^n$, where T_∞ is the constant value of T where $r=\infty$ and C and n are constants. Using this formula and a linear correction for the total height of the liquid column, absolute determinations of viscosity of very viscous media may be made with quite simple apparatus by the application of Stokes's law, the complete equation being $K=2R^2/9S(s-s')g.[T-C/(r-1)^2]$, n being taken as 2 and C depending on the diameter of the sphere, whilst s, s' are the densities of the sphere and the medium, and g the acceleration of gravity. G. F. M.

Viscosity of Binary Systems containing Stannic or Antimony Chloride. N. S. Kurnakov, S. I. Perlmutter, and F. P. Kanov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1658—1693. Compare A., 1913, ii, 190, 388; 1915, ii, 232, 423, 524).—The authors have investigated the viscosities of the binary systems formed by antimony trichloride with ethyl ether or acetone and those formed by stannic chloride with ethyl formate, acetate, or butyrate, propyl formate, ethyl benzoate, or benzene. With the exception of the system stannic chloride–benzene, each of these systems exhibits external signs of chemical action—heating of the liquid or deposition of the solid compound. The formation of the latter necessitates the choice of a suitable temperature for measuring the viscosity isotherms in the liquid condition.

With the system antimony trichloride–ethyl ether, the viscosity isotherms become increasingly flat as the temperature is raised and the maxima are displaced more and more towards the more viscous component, namely, antimony trichloride. At low temperatures the maximal viscosity corresponds approximately with the ratio $SbCl_3:Et_2O=4:1$, but, in consequence of the dissociation of the compound in the liquid state, the solid phase may be assumed to have the composition $(SbCl_3)_n,Et_2O$, where $n=2$ or 3.

For acetone the value 0·00339 is found for η_{25}; calculation from Thorpe and Rodger's results (T., 1894, 782) gives the value 0·00317, whereas Jones and Mahin (A., 1909, ii, 539, 957) found 0·00346. The general course of the viscosity curves for mixtures of acetone and antimony trichloride is similar to that observed with the preceding system. The isotherms for 50° and 80° exhibit an irrational, flat maximum for 77—80 mols. % $SbCl_3$, the position of this moving in the direction of the antimony chloride as the temperature is raised. Here, too, the existence in the liquid state of a dissociated compound, $(SbCl_3)_n,COMe_2$, where $n=2$ or 3, may be assumed.

In spite of the pronounced development of heat, sometimes as high as 5800 cals. per gram-molecule, occurring when stannic chloride is mixed with an ester of a monobasic acid, the mixtures remain liquid over considerable ranges of temperature and yield characteristic viscosity diagrams. For esters of one and the same alkyl radicle, the heat effect in these systems gradually falls as the molecular weight of the organic acid increases, the maximum viscosity undergoing a corresponding diminution. Replacement of the ethyl radicle of ethyl formate by propyl or methyl produces little change in the magnitude of the viscosity of the system. The viscosity isotherms at 25—75° and their temperature-coefficients are continuous curves with sharply marked maxima at about 33·3—40 mols. % of stannic chloride. For the system containing ethyl formate or acetate, the maxima of the viscosity diagrams correspond with 1 mol. of stannic chloride to 2 mols. of the ester. With ethyl butyrate or benzoate, however, the maxima of the isotherms are flatter and undergo displacement towards the stannic chloride as the temperature is raised from 25° to 75°, owing to increasing dissociation of the compound, $SnCl_4,2R{\cdot}CO_2Et$. The existence of these compounds is confirmed by investigating the composition of the solid phase separating on cooling the liquid solution, either by chemical analysis or by determining the distectic point in the corresponding fusion diagram. In the case of the system stannic chloride–ethyl benzoate, the fusion diagram shows, besides the distectic, $SnCl_4,2Ph{\cdot}CO_2Et$, also a maximum melting point corresponding with another solid compound, $SnCl_4,Ph{\cdot}CO_2Et$ (compare Pfeiffer, A., 1914, i, 923; ii, 568).

When stannic chloride and benzene are mixed, marked cooling takes place. The viscosity isotherms for 25° and 70° are widely different from those of the above systems and consist of almost straight lines with a slight convexity towards the axis of concentration. These results are in accord with those of Schulze and Hock (A., 1914, ii, 186) referring to the vapour pressures of the same system.

From the above results the authors conclude that the active factor determining the process of chemical interaction in these systems is the presence of oxygen in the compound with which the stannic or antimony chloride is mixed. T. H. P.

Viscosity of the System Stannic Chloride–Ethyl Propionate. N. S. Kurnakov and N. N. Beketov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1694—1701).—The existence of a singular or Dalton point in the viscosity–composition curve of a system is a necessary condition for the detection of a definite chemical compound. When the curve is continuous, the composition corresponding with the maximal point does not usually remain constant when the equilibrium factors of the system undergo change, and is not expressed by rational atomic or molecular proportions. For the system stannic chloride–ethyl propionate, the viscosity isotherms for 25° and 70° represent continuous curves with characteristic maxima at about 35 mols. % of stannic chloride. The position of the maxima is intermediate to those observed with the systems formed by stannic chloride with ethyl acetate and butyrate respectively, and the values of the maxima at 25° for the systems of this series are: ethyl formate, less than 0·6; acetate, 0·50318; propionate, 0·21400; and butyrate, 0·19828. The close approximation of the position of the maxima to the molecular ratio,

$$SnCl_4 : C_2H_5{\cdot}CO_2Et = 1 : 2,$$

indicates that the compound, $SnCl_4,2C_2H_5{\cdot}CO_2Et$, is only slightly dissociated in the liquid. This compound does indeed separate in crystals, m. p. 45·2°.

The curves connecting D_4^{25} and D_4^{70} with the composition have also been traced for this system, and are found to change in direction at points corresponding closely with the maximal viscosities.

T. H. P.

The Internal Friction of Aqueous Salt Solutions. W. Herz (*Zeitsch. anorg. Chem.*, 1917, **99**, 132—136. Compare A., 1914, ii, 338; 1915, ii, 423).—Curves are given to show that, for a number of salts of univalent and bivalent metals, the absolute fluidity is directly proportional to the specific volume of the solution. In the case of potassium and ammonium halogen salts, this is only true of higher concentrations, dilute solutions exhibiting a minimum fluidity. C. H. D.

The Adsorption of Sulphur Dioxide by Charcoal at −10°. A. M. Williams (*Proc. Roy. Soc. Edin.*, 1916, **37**, 161—172).—The relation between the pressure and the quantity of sulphur dioxide adsorbed by blood charcoal at −10° has been examined. The adsorption isotherm is of the normal type, and follows the same course as that previously found for the adsorption of water vapour.

Calorimetric observations show how the heat of adsorption at constant volume varies with the degree of adsorption. The curve expressing the relation between these quantities is of complex type and shows a minimum and a maximum, for which an explanation is offered. H. M. D.

Liquid Films in Capillary Tubes. Wilder D. Bancroft (*J. Physical Chem.*, 1917, **21**, 407—425).—Extracts from previous papers on capillary phenomena and the wetting of solids by liquids are given, and these are considered to warrant the conclusion that the rise of a liquid in a capillary tube is independent of the nature of the material of the tube provided this is wetted by the liquid. The experiments made by Bigelow and Hunter (A., 1911, ii, 471), which led these authors to the opposite conclusion, are criticised on the ground that the method which these investigators employed does not afford a measure of the adhesion of the liquid to the wall of the tube, since the liquid is not removed from the wall. It is considered that the results in question depend on the conditions which determine the displacement of a liquid from a wetted surface by air. H. M. D.

Technique of Preparing Membranes for Dialysis. William Brown (*Biochem. J.*, 1917, **11**, 40—57. Compare A., 1915, ii, 824).—The author describes the preparation of membranes of graded permeability made of collodion for use in water, chloroform, benzene, etc.; of agar and gelatin in alcohol, acetone, benzene, etc.; of formalised gelatin in water, etc. The general principle underlying the preparation of these membranes is that if a system consisting of liquid *A*–membrane substance–liquid *B* be such that (1) the membrane substance only imbibes a negligible amount of *A*, (2) the membrane substance strongly imbibes *B*, and (3) *A* and *B* are miscible in all proportions, then membranes of graded permeability for use in liquid *A* can be prepared by immersing films of the membrane substance in mixtures of *A* and *B* and transferring to liquid *A*. Graded membranes for use in liquid *B* can be prepared only when a method exists of suppressing the capacity of the membrane substance to imbibe *B*, this suppression being brought about at the stage where the membranes are still immersed in the mixture of *A* and *B*. The graded membranes of formalised gelatin are prepared in accordance with the latter method. They are found to be very useful in the purification of certain enzymes and in the investigation of phenomena of selective permeability. H. W. B.

The Selective Properties of the Copper Ferrocyanide Membrane. FRANK TINKER (*Proc. Roy. Soc.*, 1917, [*A*], **93**, 268—276).—Measurements have been made of the changes which take place in the concentration of sucrose solutions subjected to the action of colloidal copper ferrocyanide. In consequence of selective absorption of the water, the concentration of the solutions increases. The quantity of water absorbed at the ordinary temperature decreases as the strength of the sucrose solution increases, and for 100 grams of the dry ferrocyanide was found to diminish from about 30 grams for pure water to 13—14 grams for a 60% solution of sucrose. The curves showing the relation between the quantity of absorbed water and the concentration of the solution tend to become parallel to the concentration axis, and this is said to indicate the formation of a hydrate of the composition $Cu_2FeCy_6,3H_2O$, which corresponds with 15·7 parts of water per 100 of ferrocyanide. The excess quantity of water taken up from more dilute solutions is said to be adsorbed. In favour of this view, it is pointed out that there is no simple relation between the excess and the concentration of the sucrose solution, nor is the amount taken up from a given solution constant when different samples of the ferrocyanide are made use of. This variation is attributed to variations in the surface area of different samples.

The evidence afforded by these experiments is in favour of the theory that the selective permeability of colloidal membranes is the result of preferential adsorption. H. M. D.

Drainage of Crystals. NORRIS FOLGER HALL (*J. Amer. Chem. Soc.*, 1917, **39**, 1148—1152).—A mathematical paper in which the efficacy of centrifugal drainage of crystals in fractional crystallisation is considered. It is shown that the common practice of using only gravitational drainage in the case of the rare earth and similar separations is well founded, since the extra time and trouble required for centrifugal drainage would more than outweigh the relatively small gain in efficiency. On the other hand, in the separation of very dissimilar substances, especially those with flat solubility curves, the attendant great increase in the speed of purification justifies almost any amount of pains taken in washing and drainage. J. F. S.

Velocity of Crystallisation in Under-cooled Fusions. R. NACKEN (*Centr. Min.*, 1917, 191—203. Compare A., 1916, ii, 130).—Further experiments were made with salol (m. p. 41·75°). The material was crystallised between slips of glass maintained at a definite temperature by a stream of water, and observed under the microscope. The rates of growth are given for different crystal faces and edges; in each case the rate increases with the fall in temperature below the melting point. L. J. S.

The Nucleus Method for the Preparation of Colloidal Metallic Solutions of Definite Properties. Richard Zsigmondy (*Zeitsch. anorg. Chem.*, 1917, **99**, 105—117).—Colloidal solutions in which all the particles are of equal size are obtained in the case of gold ruby glass, and occasionally when the formaldehyde method is employed in the preparation of colloidal gold. Very uniform solutions are obtained by adding solutions containing nuclei, prepared by the reduction of slightly alkaline solutions of gold with phosphorus (A., 1906, ii, 679). These nuclei grow by deposition, and the number of particles is determined by the quantity of the nuclear solution added. The spontaneous formation of nuclei may be suppressed without hindering growth by the addition of ammonia or of potassium ferrocyanide or ferricyanide, whilst growth may be diminished without appreciably altering the formation of nuclei by the addition of alkali haloids, hydrogen sulphide, or colloidal sulphur.

[With C. Hiege.]—When the spontaneous formation of nuclei is suppressed by the addition of a reagent, the number of submicrons is found to be strictly proportional to the volume of the nuclear solution added, the diameter of the particles in the latter being 3·5 $\mu\mu$. Reduction with hydrogen peroxide in slightly acid solution also gives rise to very little spontaneous formation of nuclei.

[With J. Reitstötter.]—A second method is to use a solution in which growth is so rapid that the supply of gold is exhausted before the spontaneous formation of nuclei has become appreciable. Using water which has been distilled from permanganate with a gold condenser, and adding the nuclear solution to the gold chloride before adding hydroxylamine hydrochloride, with or without alkali carbonate, very clear, deep red solutions are obtained in which the number of particles is strictly proportional to the volume of nuclear solution. Blue solutions are obtained by using a larger quantity of alkali. Similar results are obtained with hydrazine, the addition of alkali being unnecessary.

Solutions of silver or mercury salts with a reducing agent, which are themselves stable, are rapidly reduced, yielding colloidal solutions when a solution containing gold nuclei is added.

C. H. D.

Effect of Freezing on certain Inorganic Hydrogels. H. W. Foote and Blair Saxton (*J. Amer. Chem. Soc.*, 1917, **39**, 1103—1125. Compare A., 1916, ii, 230).—In a previous paper it was shown that the water in moist hydrogels is present in three forms, free water, capillary water, and combined water. In the present paper the authors describe dilatometric experiments whereby the amount of combined water present has been determined. Experiments were made with the hydrogels of alumina, ferric oxide, and silica. In the case of alumina, the amount of combined water is 37·83%, whereas $Al(OH)_3$ only requires 34·6%; the excess of water is regarded as being present as a solid solution. In the case of ferric oxide, the amount of combined water present appears to depend on the method of preparation and previous treatment of the hydrogel. The results indicate that combined water is slowly given off on heating the hydrogel with water, and that there is no tendency to form compounds in which the ratio $Fe_2O_3:H_2O$ is simple. The evidence all points to the combination between ferric oxide and water being in indefinite proportions, that is, a solid solution is formed. Silicic acid hydrogels which have not been heated give fairly constant results, the combined water amounting to somewhat above 30%. On digesting with water, the amount of combined water gradually decreases until, after seven days, it reaches one mol. The evidence suggests that a part of the water in all three hydrogels is combined in indefinite proportions. A discussion is entered into as to the nature of the combined water. A few determinations of capillary water are included in the paper; in the case of alumina, the capillary water is very small in quantity, and this becomes less after freezing. In the case of ferric oxide, repeated freezing diminishes the amount of capillary water, but long-continued heating brings about the same result to a much more marked extent. In the case of silica, capillary water is not eliminated by freezing. Instead, water appears to be reabsorbed when the ice has melted. The amount of capillary water contained in silica hydrogel is decreased by digesting on a steam-bath. J. F. S.

The Sensitisation for Agglutination of Suspensoid Colloids by Non-electrolytes with Capillary Activity. H. Freundlich and P. Rona (*Biochem. Zeitsch.*, 1917, **81**, 87—106).—Substances of capillary activity, such as amyl alcohol, the urethanes, phenylthiocarbamide, camphor, and thymol, increase the flocculation sensitivity of the iron hydroxide hydrosol by electrolytes, that is to say, they cause a diminution of the concentration of the electrolytes which will cause the precipitation. This increased sensitivity can be only demonstrated when salts with univalent anions (the flocculating power of which is small), such as Cl', Br', I', NO_3', are employed. No sensitisation can be detected with the salt of greater agglutinating capacity, such as those containing F', SO_4', and citrate ions. In the case of the urethanes, the greater the capillary activity the greater the sensitising power. Substances such as camphor and thymol, which have greater capillary activity, diminish the rate of movement of the iron hydroxide sol in an electric field. The explanation of the action of the non-electrolytes is as follows. They are adsorbed on the surface of the sol particles, and in consequence of the fact that their dielectric constants are smaller than that of water, they diminish the charge on the surface. In consequence, the particles are agglutinated by smaller amounts of the ions which carry an opposite charge, and the sol is therefore precipitated by a smaller amount of electrolyte. Attention is directed to the fact that this sensitisation by non-electrolytes may play an important part in biological phenomena, and explain the precipitation of certain substances, such as nucleoproteins, by narcotics. In the latter case, the salts present are the real precipitants, the narcotics merely acting as sensitisers of the suspensoid colloids. S. B. S.

Coagulation. R. ZSIGMONDY (*Zeitsch. Elektrochem.*, 1917, **23**, 148—154).—Gold sols have been treated with measured quantities of solutions of sodium chloride, strontium chloride, aluminium nitrate, and thorium nitrate of various concentrations, and the time required for coagulation to occur has been measured. In this case, the coagulation is known to have taken place when the red solution has changed to a well-marked and easily recognised violet solution. In every case it is shown that there is a region in the concentration range of the electrolyte of minimum coagulation time. This concentration is already reached at moderate strengths ($0{\cdot}01N$—$0{\cdot}1N$) of most electrolytes. This region stretches over a considerable range of concentration, but by gradually increasing the concentration still further there is a passage into a region of slow coagulation through a somewhat narrow zone in which small changes in the concentration bring about very large changes in the coagulation time. In this region (Schwellenzone) the coagulation time lies at different places according to the time of observation. Two regions can therefore be differentiated in which a change in the concentration of the electrolyte has no effect on the stability or coagulation time of the gold sol: (1) the region below the "swelling zone," and (2) the region of greatest coagulation velocity. Both pass into one another through the region in which the coagulation time is strongly influenced by the concentration of the electrolyte. J. F. S.

Adsorptive Stratification in Gels. II. SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1917, **11**, 14—20. Compare A., 1916, ii, 474).—Experiments are described which support the view that the occurrence of stratification in gels is dependent on the number of crystallisation centres produced, and that this quantity is affected by the properties of the gel in which the reaction takes place. Solutions which produce a banded precipitate in gelatin may not do so in agar or some other medium. The extent of dilution of the reacting substances also is often an important factor in determining stratification in gels. The experiments are discussed in the light afforded by the microscopical observation of the changes occurring during stratification. H. W. B.

The Dieterici Equation of State. F. H. MACDOUGALL (*J. Amer. Chem. Soc.*, 1917, **39**, 1229—1235).—A mathematical paper in which it is shown that the Dieterici equation of state is of the correct form, and that it degenerates into the van der Waals's equation for a gas under low pressure. The equation of Dieterici might therefore be expected to have a much wider range of validity than one of the van der Waals's type. A new method of calculating a is described, and the values so obtained are compared with those calculated by other methods. The agreement between the various values in most cases is very good. J. F. S.

Direction of Spontaneous Transformations. N. V. Tancov (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1654—1658).—The author discusses the rule advanced by Ostwald (A., 1897, ii, 308), but combated by Wald (A., 1898, ii, 112), according to which, during a transition from a particular state to one of greater stability, the change is not necessarily to the most stable, but to the nearest. The conclusion now drawn from a consideration of the transformations of sulphur is that Ostwald's theory is strictly applicable only on one side of the transformation temperature, namely, below it. It is shown, further, that during spontaneous transformation at constant volume, the first condition reached is that involving the least change of the temperature-coefficient of affinity.

T. H. P.

The Curves of the Periodic Law. W. M. Thornton (*Phil. Mag.*, 1917, [vi], **34**, 70—75).—The periodic curves obtained by plotting the densities or atomic volumes of the elements as a function of the atomic weight are such that smooth curves may be drawn through the maxima or minima of the periodic curves. These smooth curves represent limiting conditions characteristic of atomic configurations, and it is suggested that the actually found periodicity affords evidence that the internal forces holding the atoms pass through a simple periodic change which in its influence on the volume of the atom is complicated by some form of structural hysteresis. H. M. D.

Simple Device for the Automatic and Intermittent Washing of Precipitates. Elbert C. Lathrop (*J. Ind. Eng. Chem.*, 1917, **9**, 527—528).—The apparatus is distinguished from the ordinary constant level device by having a capillary tube through the stopper of the inverted flask in addition to the discharge tube. The hydrostatic pressure required to pull air through the capillary when full of liquid is slightly greater than the height of the capillary rise, and consequently the level of the liquid in the funnel containing the precipitate may sink by this amount below the end of the capillary before air rushes through this into the flask and allows the liquid to discharge until the capillary end is once more covered. The flow is thus intermittent, and by selecting a suitable capillary and a discharge tube of correct length, each addition of solvent drains almost completely from the precipitate before a further quantity is automatically discharged from the container. G. F. M.

Inorganic Chemistry.

Conversion of Hypochlorite into Chlorate in Alkaline Solution. F. Foerster and P. Dolch (*Zeitsch. Elektrochem.*, 1917, **23**, 137—147).—The mechanism of the conversion of alkaline solutions of sodium hypochlorite into sodium chlorate has been studied. It is shown that at 50° the reaction is of the second order rather than the third, that is, it follows the equation $2NaClO = NaClO_2 + NaCl$ as its first stage. There is also an evolution of oxygen, which evidently occurs according to the equation $2NaClO = O_2 + 2NaCl$. The transformation of chlorite into chlorate is shown to follow the bimolecular reaction $NaClO + NaClO_2 = NaClO_3 + NaCl$. Consequently, the formation of chlorate from hypochlorite occurs according to the equations: (1) $2NaClO = NaClO_2 + NaCl$, and (2) $NaClO + NaClO_2 = NaClO_3 + NaCl$. Of these reactions, the latter occurs much more rapidly than the former. The following velocity constants have been obtained: K_1, 50° = 0·0019, 25° = 0·00010; K_2, 50° = 0·050, 25° = 0·0035. The temperature-coefficient of K_1 is 3·15, whilst that of K_2 is 2·88. The possibility of the formation of chlorite or chlorous acid in the acid decomposition of hypochlorite solutions is discussed. Carlson and Gelhaar (A., 1908, ii, 731) have stated that in the electrolytic production of chlorates, appreciable quantities of chlorites are also formed. The authors have repeated this work, and are unable to find more than the merest trace of chlorite. The fact that the chloride used by Carlson and Gelhaar has been shown to contain bromide furnishes the reason for the presence of chlorites in their experiments. J. F. S.

The Action of Iodine on the Alkalis. J. BOUGAULT (*Compt. rend.*, 1917, **164**, 949—951. Compare Péchard, A., 1899, ii, 593; Zopf, A., 1887, 688, 997).—With sodium hydroxide, iodine probably yields sodium hypoiodite, but this is so rapidly transformed into iodate that in a few minutes the reaction is almost complete. With sodium carbonate, the reactions are identical, but proceed much more slowly. With sodium hydrogen carbonate there is no apparent formation of iodate even after several days, but the presence of hypoiodite can be proved by the slow addition of sodium hyposulphite solution. W. G.

Hydrogen Sulphide Generator. F. K. BEZZENBERGER (*J. Amer. Chem. Soc.*, 1917, **39**, 1240—1241).—The apparatus described is a modification of the Ostwald generator. It consists of three large bottles, two of which are fitted with side tubulures at the bottom. The larger bottle (*A*) is the acid reservoir and is placed above the others; this is connected by its side-tube, through a valve which only permits downward flow, to the gas reservoir (*B*), and a second tube which also reaches to the bottom of *B* leads to a funnel placed in the neck of *A*. The gas reservoir is connected with the generator (*C*) by a third glass tube, and from *C* the gas is allowed to pass out through a valve similar to the one mentioned above. The main advantage of the apparatus is that the acid, when it is forced out of the generator and gas reservoir, does not pass back to the acid reservoir by the tube by which it enters; this allows the acid to be filtered through glass wool before it reaches the acid reservoir, and so prevents a large accumulation of sulphur. J. F. S.

Reaction of Sulphur Chloride with Metals. Catalytic Action of Ether. N. DOMANICKI (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1724—1727).—The investigations of Wöhler (*Annalen*, 1850, **73**, 575), Chevreul (*Compt. rend.*, 1867, **64**, 302), Baudrimont (*Compt. rend.*, 1867, **64**, 369), Smith and Oberholtzer (A., 1893, ii, 574), and Nicolardot (A., 1909, ii, 138) have shown that some metals do not react with sulphur chloride either in the cold or on heating, whilst others react only on heating, and in a few cases the reaction begins at the ordinary temperature; the products of the reaction are sulphur and chlorides of the metals, with small proportions of sulphur compounds

The author finds that the reaction may be brought about or greatly accelerated by the agency of dry ether, with which the metallic chlorides form complexes, and so enhance the thermal effect of the reaction. Under these conditions, magnesium, zinc, aluminium, tin, antimony, bismuth, molybdenum, iron, mercury, and gold are readily converted into their chlorides or etherates of the latter. On the other hand, the alkali metals, calcium, cadmium, thallium, lead, tungsten, chromium, manganese, cobalt, nickel, copper, silver, and platinum react either not at all or with extreme slowness. The metals which do react either (1) give chlorides which readily form etherates, as is the case with zinc, aluminium, tin, and bismuth, or (2) give chlorides which are readily fusible and volatile and approximate in their properties to the chloro-anhydrides; in correspondence with the latter, the higher chlorides are mostly formed, for instance, $ZrCl_4$, $FeCl_3$, $HgCl_2$. Univalent metals do not react, and bivalent metals (excepting mercury), if at all, react with far greater difficulty than ter- and quadri-valent metals. It is probable that other metals, giving volatile higher chlorides, such as titanium, germanium, vanadium, and the like, also react readily with sulphur chloride and ether. T. H. P.

The Formation of Diamonds. OTTO RUFF (*Zeitsch. anorg. Chem.*, 1917, **99**, 73—104).—The attempt has been made to repeat systematically the experiments which are stated to have led to the formation of diamonds, and especially to determine whether true equilibrium was reached by introducing small diamonds and measuring any increase. The work being broken off, it has not been possible to repeat the promising experiments of Ludwig (A., 1902, ii, 70, 451), consisting in the fusion of carbon in hydrogen under 1500 atmospheres pressure.

The products are in no cases identified with certainty as diamonds, their size being too small. For detection, the residues are heated with hydrofluoric and nitric acids on the water-bath, then with concentrated sulphuric acid and a crystal of potassium nitrate at 250°, and finally in a stream of chlorine free from oxygen at 950—1000°. Carborundum is destroyed by this process, but diamond is not attacked. Diamonds are detected by their fluorescence in ultra-violet light or α-radiation.

Small diamonds do not increase in weight when heated for fourteen days in acetylene, coal gas, methane, or carbon monoxide at temperatures up to 790°. On the other hand, a carbon arc in liquid air gives a minute residue of crystals fluorescing like diamonds. A carbon arc through which a spray of water passes continuously gives a minute residue, the fluorescence of which is very faint. Organic vapours mixed with carbon monoxide yield amorphous carbon and graphite, and mixtures of molten organic solids with catalytic agents give entirely negative results. Minute fluorescent diamonds are obtained by Moissan's method of quenching iron or its alloys with titanium, vanadium, tungsten, or molybdenum in water from 1600° or higher. At 2200° the iron on cooling is so full of graphite that there can be no internal pressure. An arc between carbon and an alloy of iron, antimony, and manganese, melting at 850°, is without effect, as is the action of acetylene or coal gas on fusible alloys, or the quenching of fused silicates in a carbon crucible.

Experiments have also been made in an electric furnace under pressures up to 3000 atmospheres, only graphite being formed.

C. H. D.

Carbon Suboxide. OTTO DIELS (*Ber.*, 1917, **50**, 753—755).—The author points out that the elaborate apparatus recently designed by Stock and Stoltzenberg (this vol., ii, 308) for obtaining larger yields of carbon suboxide offers so few advantages over his original method as to be scarcely worth while employing.

J. C. W.

The Ternary System, $H_2O-K_2SiO_3-SiO_2$.—GEORGE W. MOREY and C. N. FENNER (*J. Amer. Chem. Soc.*, 1917, **39**, 1173—1229).—The authors have studied the system $H_2O-K_2SiO_3-SiO_2$ over the temperature range 200° to above 1000°. The work comprised a determination (1) of the composition and properties of the various stable solid phases which can co-exist with solution and vapour within the above-mentioned temperature range; (2) of the composition of the solutions in equilibrium with the solid phases; (3) of the change in composition of these solutions with temperature; and (4) of the approximate corresponding three-phase pressures. In addition to quartz and the compounds $K_2Si_2O_5$ and $KHSi_2O_5$, the following new compounds occur as solid phases: potassium disilicate monohydrate, $K_2Si_2O_5,H_2O$; potassium metasilicate, K_2SiO_3; potassium metasilicate hemihydrate,

$$K_2SiO_3,0{\cdot}5H_2O;$$

and potassium metasilicate monohydrate, K_2SiO_3,H_2O. The experimental data are presented by means of tables and graphically by means of curves and photographs of solid models. Curves are given showing (1) the solubility relations in the binary systems $H_2O-K_2SiO_3$ and $H_2O-K_2Si_2O_5$; (2) the isothermal polybaric saturation curves; (3) the variation of pressure with the ratio $SiO_2:K_2O$ along the isotherms; (4) the isobaric polythermal saturation curves; (5) the $P.T$ curves of the various univariant systems; and (6) the boundary curves of the different solid phases in the ternary system. In addition, photographs are given of the solid models showing the variation in the composition of the saturated solutions with temperature, and under the corresponding three-phase pressure, and also the variation of the composition of the saturated solutions with pressure at the corresponding three-phase temperatures. A short discussion is entered into in connexion with some of the theoretical relations governing the equilibrium in binary and ternary systems containing a volatile component, and also of the proper application of the term "solubility." J. F. S.

The Course of the Reaction between Silver and Sulphides (Hepar Test). Friedrich L. Hahn (*Zeitsch. anorg. Chem.*, 1917, **99**, 118—122).—The blackening of metallic silver by hydrogen sulphide or soluble sulphides, used as a qualitative test for sulphur, is sometimes represented as taking place in the absence of air, with liberation of hydrogen, and sometimes as a reaction with oxygen, the former hypothesis being adopted in most recent text-books.

When precautions are taken to exclude air, silver may be boiled for hours with sodium sulphide solution without evolution of hydrogen, the metal being unchanged, blackening taking place immediately air is admitted. Hydrogen sulphide may also be passed through water in which silver is placed without any blackening. The presence of oxygen or hydrogen peroxide causes immediate blackening. C. H. D.

Properties of Barium Sulphate. Z. Karaoglanow (*Zeit. anal. Chem.*, 1917, **56**, 225—246).—See this vol., ii, 387.

Contamination of Precipitates in Gravimetric Analysis. Solid Solution and Adsorption versus Higher Order Compounds. George McPhail Smith (*J. Amer. Chem. Soc.*, 1917, **39**, 1152—1173).—A number of experiments have been carried out on the nature of the material carried down with the precipitate when sulphuric acid or sulphates are treated with barium chloride in the presence of ferric iron. In all cases it is shown that considerable quantities of iron are included in the precipitate; of the various hypotheses which have been put forward to account for such inclusions, the author, from the results of the experiments, favours the view that an insoluble complex ferric barium sulphate is formed, so that there is neither adsorption of ferric compounds nor the formation of solid solutions, but rather the formation of barium ferric sulphate, $Ba[Fe(SO_4)_2]_2,nH_2O$, which is insoluble and admixed with the barium sulphate. Although disulphatoferric acid and its alkali salts are known, attempts, which are described in the paper, to prepare the alkaline earth salts of this acid failed. J. F. S.

Example of a Reversible Reaction and Complex Salt Formation. K. Elbs (*Zeitsch. Elektrochem.*, 1917, **23**, 147—148).—A series of experiments is described to show that the reaction $CuI_2 \rightleftarrows CuI+I$ is really a reversible reaction. The reaction can be made to proceed entirely from left to right by removal of the iodine with thiosulphate, that is, the change $Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot}$ is complete. If the cupric ions are removed, it is obvious that the reaction must proceed from right to left; this may be achieved by adding to the mixture of cuprous iodide and iodine a salt which forms complexes with the cupric ion. Ammonium oxalate serves this purpose, and if ammonium oxalate is added to the mixture of cuprous iodide and iodine, an intensely blue solution of cupric ammonium oxalate is formed. J. F. S.

Influence of the Velocity of Cooling on the Temperature of Transformation and Structure of Carbon Steels. A. Portevin and Garvin (*Compt. rend.*, 1917, **164**, 885—888).—For a given steel and a given initial temperature of tempering, the lowering of the transformation point is not parallel to the increase in the velocity of cooling. The transformation, well marked at high temperatures on the curve, disappears suddenly at low temperatures, and then can only be observed by comparison with a metal having no transformation point. There are thus critical values for the velocity of cooling which mark the change in the position and the form of the transformation. With transformation at high temperatures troostite is obtained, and at low temperatures martensite. In steels other than the eutectic, the troostite is always accompanied by some proeutectic constituent. When troostite and martensite exist simultaneously, the curve shows an irregularity both at high and low temperatures. A rise in the initial temperature for given conditions of tempering tends to displace the transformation at low temperatures. The critical value of the velocity of cooling for a given initial temperature depends on the composition of the steel. It does not always vary in the same sense as the carbon content, and appears to have a minimum at the eutectic content. W. G.

Anomaly of Cementite in Carbon Steels, Annealed, Tempered, and Half-tempered. P. Chevenard (*Compt. rend.*, 1917, **164**, 1005—1008).—The magnetic transformation of the cementite in carbon steels (compare Wologdine, A., 1909, ii, 374) is accompanied by a change in direction of the dilatation curve. Measurements have been made on nine steels, and the differential curves obtained show an irregularity of negative expansion comparable with the negative anomaly of the ferronickels of the group Fe_2Ni. For all the steels, the transformation point was at 210°, which coincides with the temperature of sudden fall of magnetisation of cementite obtained by Honda and Tagaki (compare A., 1916, ii, 105). A study of this irregularity of the cementite can be used to determine the state of the carbon in steels after treatment, and the method has been applied to a steel containing 0·83% carbon tempered at 800° in cold water. W. G.

Iron and Boron. N. Tschischevsky and A. Herdt (*Rev. Soc. russe Met.*, 1915, **1**, 533—546; from *J. Soc. Chem. Ind.*, 1917, **36**, 650).—Iron–boron alloys containing up to 11·54% of the latter were prepared from pure Swedish iron and ferroboron, and their cooling curves determined. For micrographic determinations, the specimens were cooled slowly and etched with a solution of sodium picrate. The eutectic alloys presented the appearance of pearlite (boron–pearlite) to a greater degree than the corresponding carbon steels. With 0·08% boron, continuous masses of ferrite were exhibited surrounded by thin lines of pearlite; the latter gradually widened and extended as the boron content increased until the eutectic composition and the maximum of pearlite were reached with 3·1% of boron. With 3·5% of boron, the formation of prismatic boride crystals (boron–cementite) commenced; these increased with the boron content, and finally agglomerated into masses separated by veins of eutectic. Polished sections of alloys containing more than 8% of boron were prepared only with difficulty, owing to general brittleness and lack of cohesion. The 8·85% alloy consisted of a mass of long, prismatic crystals of the composition Fe_2B. The results of the chemical, thermal, and micrographic analyses are shown in a diagram. H. W.

Explosive Property of Uranyl Nitrate. II. Arno Müller (*Chem. Zeit.*, 1917, **41**, 439. Compare A., 1916, ii, 143).—In order to elucidate the apparently arbitrary conditions under which explosive specimens of uranyl nitrate may be formed, ethereal solutions containing free nitric acid or nitric oxide, or without added agent, have been allowed to crystallise while under the influence of the Röntgen rays, but no effect on the crystals could be observed. The conclusion is therefore drawn that it is not the accidental presence of radium which imparts the explosive property to uranyl nitrate. J. C. W.

Preparation of Black Oxide of Uranium (UO_2). Charles L. Parsons (*J. Ind. Eng. Chem.*, 1917, **9**, 466—467).—Black uranium oxide was prepared on a technical scale by fusing 35 parts of sodium chloride, 20 parts of sodium uranate, and 1 part of powdered charcoal in a cast steel pot. Reaction occurs at a red heat, and is allowed to continue until the escape of gas ceases. The cooled mass was lixiviated with water, and the heavy uranium oxide settled on the bottom of the tank and was washed by decantation. It may be freed from iron and aluminium compounds if necessary by treatment with 5% hydrochloric acid, and in commercial practice a purity equivalent to 97% U_3O_8 is easily obtained. Vanadium, if present, is recovered as a by-product, going into solution as sodium vanadate, and being precipitated therefrom by ferrous sulphate. In general, no attempt was made to separate all the iron, since its presence was not deleterious in the production of ferro-uranium. G. F. M.

The Preparation in a Pure State of Highly Reactive Metals and Metalloids. Emil Podzus (*Zeitsch. anorg. Chem.*, 1917, **99**, 123—131).—For the preparation of titanium and zirconium, a steel bomb is used, closed by a strong screw and sealed with molten lead. The reduction mixture, consisting of sodium and titanium chloride or potassium zirconifluoride, is introduced in an atmosphere of hydrogen or carbon monoxide, several clean iron balls being added. The bomb being closed, the whole is revolved for twenty to forty hours at about 200° to bring about an intimate mixture. Heating strongly for a few minutes starts the reaction. When a large excess of sodium is used, vapour may escape through the lead seal. The bomb is cooled from the top downwards, so that the lead may be solid before the pressure falls. The element is obtained in a minutely crystalline, highly reactive form, titanium being 99·7% and zirconium 99·3%. The method fails to give pure boron.

Apparatus is described for the preparation and purification of boron trichloride. Reduction with sodium, even in a vessel of pure boron nitride electrically heated by a resistance spiral of boron and boron carbide, yields only a black powder which will not weld to a compact mass. Iron is found to give the best results. Wire, prepared by drawing down Kahlbaum's pure iron, is wound on a frame made of boron nitride, and heated by means of a resistance tube of boron and boron carbide enclosed in a large glass vessel with mercury seals. The leading-in wires are of tungsten. After filling with hydrogen, the furnace is heated to redness to remove traces of oxygen. Hydrogen is then expelled by filling with boron trichloride. Most of the reduction takes place at about 800°, and the temperature is then raised gradually to 1700°. A porous mass of pure boron is thus obtained, which becomes denser on prolonged heating in boron trichloride. Compact boron thus prepared has an appreciable conductivity and is very infusible, an arc struck between boron poles showing no trace of fusion unless iron is present. The wires may be heated electrically to bright whiteness without injury. C. H. D.

The Zirconyl Sulphates. Ed. Chauvenet (*Compt. rend.*, 1917, **164**, 946—949. Compare this vol., ii, 322).—The author gives graphic formulæ showing the six zirconium sulphates as derivatives of the zirconyl radicle, which he considers them to be. The various hydrates of these sulphates are tabulated. W. G.

Double Salts of Bismuth Trichloride and Chlorides of Bivalent Metals. R. F. Weinland, A. Alber, and J. Schweiger (*Arch. Pharm.*, 1916, **254**, 521—536).—Bismuth chloride, prepared from the hydrated nitrate, is dissolved in the smallest possible quantity of concentrated hydrochloric acid, and the solution is treated with the carbonate or hydroxide, or in a few cases the chloride of the bivalent metal. The latter was added in some cases so long as it dissolved, in other cases in amounts less than this. In no case did the solution of bismuth chloride (1 mol.) dissolve more than 1 mol. of the bivalent chloride. The solutions were then concentrated over sulphuric acid until the double salts crystallised. The double salts obtained are colourless (except when a coloured cation has been added), hygroscopic, and are decomposed by water, bismuth oxychloride being precipitated. Three series of salts have been obtained: (1) $BiCl_3,M''Cl_2$, obtained when the solution of bismuth chloride has dissolved the maximal amount of carbonate or hydroxide. Such salts are: $M''=Mg$, stout, rectangular plates with $8H_2O$; $M''=Ca$, plates with $7H_2O$; $M''=Sr$, rectangular, four-sided plates with $8H_2O$; $M''=Ba$, rhombic plates with $4H_2O$; $M''=Co$, pale red prisms with $6H_2O$; and $M''=Ni$, green needles with $6H_2O$. These salts correspond with the series $BiCl_3,2M'Cl$, where M' is an alkali metal, and are regarded as derivatives of pentachlorobismuthic acid, $H_2[BiCl_5]$. (2) $2BiCl_3,M''Cl_2$, obtained generally from solutions in which the molecular ratio of bismuth chloride to bivalent chloride is 10:4 or 10:2. Such salts are: $M''=Ca$, colourless needles with $7H_2O$; $M''=Sr$, stout needles with $7H_2O$; and $M''=Ba$, slender needles with $5H_2O$. They correspond with the series $BiCl_3,M'Cl$ (M'=alkali metal), and are regarded as derivatives of tetrachlorobismuthic acid, $H[BiCl_4]$. (3) $4BiCl_3,M''Cl_2$, obtained generally when the molecular ratio of bismuth chloride to bivalent chloride is 10:1. Such salts are: $M''=Mg$, six-sided leaflets with $16H_2O$; $M''=Sr$, six-sided leaflets with $12H_2O$; $M''=Mn$, flesh-coloured, six-sided plates with $12H_2O$; $M''=Fe$, faintly yellowish-red plates with $12H_2O$ (the colour is probably modified by the presence of a little ferric salt); $M''=Co$, red, six-sided plates with $12H_2O$; and $M''=Ni$, pale green, six-sided plates with $12H_2O$. These salts correspond with the series $2BiCl_3,M'Cl$ (M'=alkali metal), and are regarded as derivatives of heptachlorodibismuthic acid, $H[Bi_2Cl_7]$.

The distribution of the water in the double salts is discussed from the point of view of the co-ordination theory. C. S.

Colloidal Metals of the Platinum Group. IV. Colloidal Iridium. C. Paal (*Ber.*, 1917, **50**, 722—737. Compare A., 1904, ii, 180).—Directions are given for the preparation of iridium hydrosols which may be safely dried, by reduction of alkaline iridium solutions with hydrogen, hydrazine hydrate, sodium formate, or formaldehyde, in the presence of sodium protalbate or lysalbate as protective colloid.

Technical iridium chloride, which is the available starting material, is a mixture of the tetrachloride with some trichloride. It is slightly hydrolysed by water, and clear solutions are only obtained by the addition of hydrochloric acid. When the solution is added to solutions of the protective colloid, olive-green or rust-brown precipitates of the protalbate or lysalbate are produced, the colour being dependent, apparently, on the amount of free hydrochloric acid. These precipitates dissolve in sodium carbonate or hydroxide to form the blood-red hydrosols of iridium trihydroxide. With an excess of sodium hydroxide, the sol suffers oxidation on exposure to the air, giving the blue hydrosol of iridium tetrahydroxide. The iridium hydrosols obtained from these by reduction are of different degrees of sensitiveness towards electrolytes. With sodium formate or formaldehyde, the undialysed hydroxide sols may be safely used, but dialysis must precede any application of hydrazine as the reducing agent or any attempt to prepare concentrated iridium sols. If the sol with sodium lysalbate as the protective colloid is acidified, some of the lysalbic acid is left in solution and the gel therefore enriched in iridium. By redissolving this in sodium hydroxide and repeating the process a few times, a sol may be obtained which, on drying, contains as much as 73% of iridium.

The solutions employed contain 1% of iridium as chloride and 1% of the protective salts. During the final dialysis, a small quantity of alkali is lost, owing to the hydrolysis of the protective salts, so it is advisable to replenish this before evaporating the sol.

[With FERD. BIEHLER and HERMANN STEYER.]—The reduction with sodium formate in the presence of sodium protalbate and lysalbate is described. The dry preparations formed black, glistening, friable lamellæ, which redissolved almost completely after a year or so, and contained from 30—42% of iridium.

[With HERM. STEYER.]—Reductions with formaldehyde, hydrazine hydrate, and gaseous hydrogen are described. J. C. W.

Mineralogical Chemistry.

Palæophysiology: the Organic Origin of some Minerals Occurring in Sedimentary Rocks. J. V. SAMOILOV (*Min. Mag.*, 1917, **18**, 87—98).—In connexion with the exploration of the phosphate deposits of Russia, the occurrence of barytes has been noted over a wide area in the governments of Kostroma, Kazan, and Simbirsk, whilst still farther to the north-east similar deposits of barytes have been met with in the basin of the Pechora River. The mineral occurs as nodules in the clays and marls of the Upper Jurassic, and is confined to the Oxfordian-Sequanian horizon, though in some of the districts it extends up into the Kimeridgian. Nodules of barytes have been dredged from the sea-floor off the coast of Ceylon, and granules of barium sulphate have been detected in the bodies of certain marine organisms, namely, the Xenophyophora. If, therefore, during the Upper Jurassic period such organisms, capable of extracting barium salts from sea-water, were more abundant, they would account for the accumulation of barium in these strata, where the barytes occurs as a primary mineral.

Similarly, the mineral celestite has been found over a very wide area in Turkestan in beds of Upper Cretaceous age. The presence of strontium sulphate has been detected in the skeletons of the Acantharia, a group of the Radiolaria. It is conceivable that similar organisms were relatively more abundant during the Cretaceous period, and that their remains gave rise to the deposits of celestite.

Although the iron compound hæmoglobin plays an important function in the blood of present-day animals, yet cases are known amongst the Crustacea and Mollusca in which the copper compound hæmocyanin performs the same function; and vanadium has been detected in the blood of the Ascidia. During former periods of the earth's history these, and perhaps some other, metals may have predominated in the blood of animals then living. In this connexion, the persistent occurrence in the Permian strata of copper minerals and ores associated with abundant animal remains is significant. In the same way there may have been at different periods variations in the chemical composition of the ash of plants.

The recurring presence of minerals of primary origin in certain sedimentary strata therefore suggests that there may have been varying physiological processes during past periods, and for this new branch of palæontology the name palæophysiology is suggested.

L. J. S.

Cyanotrichite and Dioptase from Traversella. LUIGI COLOMBA (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 487—491).—Small stalactites and thin incrustations coating some of the rock in a gallery of one of the Traversella mines were found to consist of either very thin plates aggregated so as to form a radiating structure about the axis of the stalactites or minute acicular crystals which tend towards a lamellar habit when their dimensions increase. Both the plates and needles are colourless under the microscope, but thicker aggregates exhibit a greenish-blue colour with no trace of pleochroism. They contain a little calcium, apparently as contamination in the form of gypsum, and if an allowance is made for this, the percentage composition is as follows:

CuO.	Al_2O_3.	SO_3.	H_2O (by diff.)
53·05	8·72	12·11	26·12

The mineral is hence a variety of cyanotrichite, differing from other minerals known as cyanotrichite and woodwardite in its high content of water and its poorness in aluminium.

The stalactites also contain isolated individual masses or dendritic forms of an emerald-green mineral, which forms moderately hard, prismatic crystals, and appears to be dioptase.

T. H. P.

Tapiolite from Western Australia. EDWARD S. SIMPSON (*Min. Mag.*, 1917, **18**, 107—121).—Crystals of tapiolite ($FeTa_2O_6$) are described from Tabba-Tabba Creek and from Greens Well, in the Pilbara goldfield. They are tetragonal ($a:c=1:0·6539$), and by twinning simulate monoclinic symmetry. The density of different crystals ranges from 7·36 to 7·907; the latter value, being the highest recorded, is assumed to represent the density of pure iron tantalate (the value for the corresponding columbate, mossite, being set at 5·20). Analysis of a crystal (D 7·45) from Tabba-Tabba Creek gave:

Ta_2O_5.	Cb_2O_5.	TiO_2.	SnO_2.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.
82·55	1·37	0·18	0·34	0·83	10·69	1·49	1·96	0·10	0·31	99·82

L. J. S.

Magnesian Tourmaline from Renfrew, Ontario. E. L. Bruce (*Min. Mag.*, 1917, **18**, 133—135).—Reddish-brown crystals and grains occur in limestone and in granite-gneiss near the contact of the two rocks in a limestone quarry near the town of Renfrew. The mineral encloses much graphite and calcite; analysis of carefully selected material, D 3·07, gave:

SiO_2.	B_2O_3.	Al_2O_3.	Fe_2O_3.	FeO.	TiO_2.	CaO.	MgO.	K_2O.	Na_2O.	F.	H_2O.	Total less O for F.
35·29	10·56	28·93	2·35	0·70	0·025	5·49	14·53	0·22	1·72	0·84	0·70	101·00

These results agree with the formula $H_{18}(BOH)_2Si_4O_{19}$ of Penfield and Foote (A., 1899, ii, 304). L. J. S.

Composition of Pyroxenes. C. Doelter (*Centr. Min.*, 1917, 185—191).—A criticism of the recent papers by Boeke (A., 1911, ii, 283), Zambonini (A., 1915, ii, 570), and Tschermak (A., 1916, ii, 145). Little definite evidence can be adduced either for or against the various hypothetical components assumed by these authors. Further experimental work is needed in the direction of the preparation of possible components and their miscibility.

L. J. S.

Analytical Chemistry.

Simple Device for Evaporating Solutions to a Definite Volume. G. P. Plaisance and N. C. Pervier (*J. Amer. Chem. Soc.*, 1917, **39**, 1238—1241).—A device is described by which a number of solutions may be evaporated to any required volume without any attention. The apparatus works on the principle of a balance; a plate of metal perforated with nine holes of slightly larger diameter than a beaker is hung from a pair of metal rods. The rods work on knife edges supported by a metal stand, and are balanced at the far end by weights. The beakers, of the same size, are filled with the same volume of liquid and rest on a hot-plate or water-bath; suitable weights are placed on the other arm. When sufficient of the liquid has evaporated, the beakers are raised from the hot-plate by the weights and brought against a large glass slab, which serves the double purpose of covering the beakers and preventing them being raised too much. J. F. S.

Apparatus for the Reduction of Volume of Gases to Standard Temperature and Pressure. A. V. C. Fenby (*Chem. News*, 1917, **116**, 5—8).—A mechanical device designed to facilitate the reduction of the volumes of gases, measured at known temperatures and pressures, to normal temperature and pressure. Three different forms of the instrument are described, one of these being of the ordinary slide-rule pattern and one a circular form.

H. M. D.

Improved Compensator for Gas Analysis. E. T. Gregg (*J. Ind. Eng. Chem.*, 1917, **9**, 528).—An improved compensator is described for use in conjunction with the Hempel apparatus to adjust the pressure of the gas in the burette before taking a reading. It depends on the making of a mercury platinum contact in a U-shaped manometer connected with the burette on the one hand and a compensator bulb on the other. The contact forms part of a circuit in which are included a small dry cell, a switch, and a miniature lamp, and the volume of the gas in the burette is adjusted by means of a mercury levelling bottle until the lamp glows. It is claimed that this arrangement gives more accurate results in less time and with less strain on the eyes of the operator than the usual optical method of adjusting the mercury to a mark.

G. F. M.

Titration of Chlorides by Mohr's Method, and its Application to the Examination of Potable Water. I. M. Kolthoff (*Pharm. Weekblad*, 1917, **54**, 612—618).—The best proportion of chromate in the titration of chlorides is 0·7—1 c.c. per 100 c.c. of liquid. The end-point is more readily observed in artificial light than in daylight. The presence of free acid, phosphates, and ferrous and ferric salts interferes with the sensitiveness of the reaction, but borax has no effect. A. J. W.

Volumetric Estimation of Sulphur in Pyrites. Harcourt Phillips (*Chem. News*, 1917, **115**, 312).—A description of a rapid method for the estimation of sulphur in pyrites, based on the use of a standard solution of barium chloride, of which 1 c.c. is equivalent to 0·01 gram of sulphur. A deficient quantity of barium chloride solution is added to the oxidised pyrites solution which has been freed from nitric acid and has been adjusted to a definite bulk; the titration is completed by making further additions of 0·5 c.c., boiling the liquid, and filtering off 5 c.c. after each addition, the end-point being reached when this hot filtrate fails to give a turbidity in three minutes after the addition of two more drops of the barium chloride solution.

The barium chloride solution is standardised under similar conditions against a solution of sulphuric acid made to contain the equivalent of 0·01 gram of sulphur per c.c. D. F. T.

Detection and Estimation of Sulphur in Petroleum. C. K. Francis and C. W. Crawford (*J. Ind. Eng. Chem.*, 1917, **9**, 479—481).—E. Fischer's methylene-blue test provides the most delicate method for the detection of sulphur in petroleum. The sulphur is converted into sodium sulphide by treating the oil with sodium in the usual way, and in the filtered solution, slightly acidified with hydrochloric acid, a crystal of *p*-aminodimethylaniline sulphate is dissolved. A few drops of ferric chloride solution are then added, and the formation of a blue coloration indicates the presence of sulphur. No sulphur as hydrogen sulphide or carbon disulphide was found in the Cushing oil (Bartlesville sand), but alkyl sulphides and thiophens were present. Hydrogen sulphide was formed when the oil was heated above 225°. For the quantitative estimation of sulphur, the Eschka method was not applicable, but by fusion with sodium peroxide and potassium chlorate in a bomb and estimation as sulphate, accurate results were obtained. A modified Dammer combustion method (*Zeitsch. angew. Chem.*, 1911, **22**, 400), using catalytic oxidation with platinum spirals and absorption of the oxides of sulphur in hydrogen peroxide, also gave concordant results, but required greater care and vigilance than the peroxide method. G. F. M.

The Use of Potassium Persulphate in the Estimation of Total Nitrogen in Urine. LEONARD C. SCOTT and ROLLIN G. MYERS (*J. Amer. Chem. Soc.*, 1917, **39**, 1044—1051. Compare Huguet, A., 1910, ii, 155).—A comparison of the macro- and micro-chemical methods of estimating total nitrogen in urine, replacing potassium sulphate by the persulphate, free from nitrogen. In the macrochemical method, 5 c.c. of the urine, 10 c.c. of sulphuric acid, and 10 c.c. of a 2·5% solution of copper sulphate are boiled until the liquid is yellow. The flask is allowed to cool and 1·5—2·0 grams of potassium sulphate added, and the liquid reheated until the action begins. The flask is removed from the flame and rotated until the solution is colourless, being finally reheated until all sulphur trioxide is driven off. The estimation of nitrogen is then made as in the ordinary Kjeldahl process. In the microchemical method, the procedure recommended by Folin and Farmer (compare A., 1912, ii, 702) is followed, using the persulphate instead of the sulphate, and finally driving off all the sulphur trioxide as above. Both these methods are rapid and yield results which agree with those obtained by the Arnold-Gunning method taken as a standard. In the micro-method, all traces of calcium and magnesium must be eliminated from the water used for the dilutions. W. G.

Estimation of Ammonia in the Soil and in Liquid Manure. W. J. BARAGIOLA and O. SCHUPPLI (*Landw. Versuchs-Stat.*, 1917, **90**, 123—137).—The ammonia present in the soil may be estimated as follows: 50—100 grams of the soil are mixed with 5—7 grams of magnesium oxide, and at once introduced into a Claisen (two-necked) fractionating flask holding about three-quarters of a litre, together with about 100 c.c. of water. The flask is connected with a bulbed tube passing tightly through the stopper of a pump flask which contains 10—20 c.c. of *N*/5-sulphuric acid, and is surrounded by ice-water. The side-tube of the pump flask is connected with that of a second, which serves as a safety flask, and is joined to a water-pump and also carries a manometer. A tube drawn out at the bottom to a capillary and connected above with a sulphuric acid washing bottle passes almost to the bottom of the distillation flask.

The pressure is lowered to about 15 mm. and the water-bath in which the distillation flask is immersed heated to about 35°. The distillation is continued until the residue is dry, this requiring about two hours. A slow current of ammonia-free air is then passed for a time through the flask. The contents of the receiver are finally washed out into an Erlenmeyer flask, boiled to expel carbon dioxide, and when cold titrated with *N*/10-sodium hydroxide in presence of Congo-red; the titration is carried on until the colour matches that given by a mixture of the same volume of *N*/5-sulphuric acid as is used in the test with an equivalent volume of *N*/10-sodium hydroxide.

Under the above conditions, not only ammonia, but also volatile amines and other bases, pass over, and the ammonia may be separated in the following manner. Either a fresh distillate, obtained as above, or an aliquot part of the original distillate before addition of Congo-red, is treated in a beaker with 1 c.c. of concentrated hydrochloric acid and 10 grams of sodium acetate and 12 grams of sodium phosphate dissolved in the liquid; the sparingly soluble phosphate may with advantage be dissolved separately in a little hot water and the cooled solution added to the liquid. After further addition of 15 c.c. of 10% magnesium chloride solution, a little phenolphthalein, and a pinch of quartz sand, the whole is vigorously stirred mechanically by means of a water-turbine. Sodium hydroxide solution is slowly added from a dropping funnel until a persistent, faint pink coloration is reached. After about fifteen minutes, the amorphous, gelatinous precipitate assumes a crystalline form, the pink colour disappearing. A further addition of sodium hydroxide solution is made until the liquid again remains pink, and the liquid then kept stirred for fifteen minutes longer. If too much sodium hydroxide is accidentally added and danger of decomposition of the magnesium ammonium phosphate into trimagnesium phosphate and ammonia thus incurred, hydrochloric acid should be added and then the alkali until the proper end-point is reached. The stirring should last altogether about half an hour. The solution is allowed to settle for a short time and then filtered through a Neubauer platinum crucible or a porcelain Gooch crucible, the heavier quartz sand being left in the beaker and subsequently washed, together with the precipitate on the filter, with a total of about 25 c.c. of 3% sodium acetate solution. The precipitate adhering to the sand and also that on the filter is dissolved in dilute hydrochloric acid, the solution being afterwards distilled with excess of sodium hydroxide solution and the ammonia collected in standard sulphuric acid and estimated by titration with sodium hydroxide in presence of Congo-red.

The ammonia which passes over when soil is distilled with magnesium oxide seems to be that actually existing as ammonium salts in the soil, since after some time it disappears, having undergone complete conversion into nitrate.

The above method is applicable also to liquid manure, 50 c.c. of the latter and 10 grams of magnesium oxide being taken, and the distillate made up to a definite volume and aliquot portions used for the direct titration of the volatile basic nitrogen and for the precipitation of the ammonia as magnesium ammonium phosphate.

Both in soil and in liquid manure, direct titration of the distillate obtained as above and that from the magnesium ammonium phosphate gives virtually identical values, so that amines and volatile bases other than ammonia pass over only in negligible quantity. T. H. P.

A Precipitant for Nitrous Acid. Friedrich L. Hahn (*Ber.*, 1917, **50**, 705—708).—2:4-Diamino-6-hydroxypyrimidine (Traube, A., 1900, i, 416) is an excellent precipitant for nitrites, giving a precipitate with as little as 0·05 mg. NO_2' per c.c., and a coloration with as little as 0·015 mg. The precipitate cannot be used for quantitative estimations of nitrites, but the process is particularly useful for detecting nitrates in nitrites. The sparingly soluble sulphate is the best salt to employ, as the excess of reagent largely crystallises out in the cold, and nitrates can then be estimated undisturbed in the filtrate by means of "nitron" or detected with the usual sensitiveness by means of diphenylamine or ferrous sulphate. J. C. W.

Application of the Gutzeit Test to Works Estimation of Arsenic. C. Hollins (*J. Soc. Chem. Ind.*, 1917, **36**, 576—577).—An apparatus is described and figured which has proved useful in examining the quality of dearsenicated vitriols, and is also applicable to the estimation of arsenic in phosphates, phosphoric acid, and other substances containing only small quantities of arsenic. It consists of a wide-mouthed bottle of about 100 c.c. capacity fitted with a two-holed rubber bung. One hole supports a short tube bent at right angles and closed by a cap; the other supports a tube of 4—5 mm. internal diameter on which three bulbs are blown, the first two of which contain a little lead acetate solution (10—20%), whilst the third is tightly packed with glass wool wetted with the same solution; the third bulb is connected to a tube inclined at an angle of 45°, which contains the mercuric chloride paper (10 cm. long). The latter is best prepared by soaking Michallet drawing paper in water until limp, and then keeping it moving in mercuric chloride solution (1%) for half an hour. The sheets are drained and dried separately in the steam-oven. They can then be preserved for two or three months in the dark in a test-tube fitted with a rubber bung.

A series of standard stains is prepared with known amounts of arsenic. These are trustworthy for about three months if preserved with phosphoric oxide in sealed tubes and exposed to light as little as possible. The sensitiveness of a new batch of papers must, however, always be tested by preparing two or three standards from it.

In performing the test, 40 c.c. of water are placed in the flask, a measured volume of the vitriol (0·5—2·0 c.c.), and sufficient arsenic-free sulphuric acid to make up the total acid to 2 c.c. (D 1·84) are added. Three drops of arsenic-free stannous chloride solution are introduced, the paper slip is placed in the tube, and 3—4 grams of arsenic-free zinc are added. After half an hour the stains are compared with the standards.

The most accurate results with 1% mercuric chloride paper are given by stains of between 7 and 20 micromilligrams. With stains of 35 or less, there is no loss of arsenic hydride. Under certain conditions of dilution, appreciable quantities of hydrogen sulphide are evolved, but the test is trustworthy if the glass wool is not blackened. The time occupied by a single estimation is less than thirty-five minutes.

A stain which is otherwise invisible may be developed by touching the paper with a drop of concentrated hydrochloric acid. A stain which is just visible on development represents about 0·05 micromilligram of arsenious oxide.

The sensitiveness of the test paper is diminished by using concentrated solutions of mercuric chloride, but does not increase on dilution beyond 0·5%. Paper prepared with 1% solution is nearly three times as sensitive as that prepared with a saturated solution.

H. W.

The Estimation of Boric Acid in Special Glasses. Paul Nicolardot and Jean Boudet (*Bull. Soc. chim.*, 1917, [iv], **21**, 97—101).—Slight modifications are introduced into the method of Hönig and Spitz (compare A., 1917, ii, 159). It is necessary to exclude all carbon dioxide from the solutions prior to titration in the presence of glycerol or mannitol with phenolphthalein as indicator, and all ammonium salts must be driven off. Magnesium and aluminium, in amounts greater than those which exist in special glasses, do not interfere with the estimation or retain any boric acid.

Provided that the material is first thoroughly fused with alkalis, the method of estimating boron, by distillation as methyl borate, is satisfactory.

W. G.

Experiences with Mandel and Neuberg's Catalytic Method for Elementary Analysis. Th. Merl and K. Lüft (*Zeitsch. Nahr. Genussm.*, 1917, **33**, 384—388).—The authors describe the application of Mandel and Neuberg's method (oxidation with 15% hydrogen peroxide in the presence of a small quantity of iron. A., 1915, ii, 788) to the estimation of sulphur in "saccharin" and bromine in the bromine derivatives of higher fatty acids, and find it most satisfactory. The method also serves well as a preliminary test for "saccharin" on the ether–light petroleum extract obtained in a systematic analysis. Within a few minutes it is possible to obtain from less than a milligram of the substance distinct evidence of the oxidation products, sulphuric acid, ammonia, and benzoic acid. J. C. W.

The Analysis of Coal, and a New Scheme for the Examination of Coal. H. Gröppel (*Chem. Zeit.*, 1917, **41**, 413—414, 431—434).—The author discusses the methods which have been used and are now in common practice for estimating moisture, yield of coke or volatile products, and ash in coal, and directs attention to their respective merits and failings.

A new procedure is recommended, in which the moisture, coke, and ash are estimated with the same weight of coal in the same apparatus, a bent, hard glass tube ("duck"-shaped). For the estimation of moisture, the tube is connected to weighed calcium chloride tubes, the bend is immersed in a bath at 105°, and dry hydrogen is passed through. After removing the drying tubes, the coal is then coked in the current of hydrogen, and finally burnt in a stream of oxygen for the ash determination. As an alternative, the combustion tube may be sealed to a tube bent into two parallel U's, the second of which is filled with glass beads. With this, the dried coal is coked and the tar and water absorbed in the bent tubes, which are cooled. The coking tube is then severed, and so the weights of coke and of tar + water, and consequently of gas, can be obtained. J. C. W.

The "New" Method of Gad-Andresen for Estimation of Carbon Monoxide in the Blood. N. Zuntz (*Biochem. Zeitsch.*, 1916, **78**, 231—232).—The method described by Gad-Andresen (A., 1916, ii, 447) does not differ in essentials from that previously described by the author and J. Plesch (*Biochem. Zeitsch.*, **11**, 47). S. B. S.

Apparatus for Estimating the Noble Gases [Argon, etc.] and Nitrogen by a Gas-analysis Method. R. Brandt (D.R.-P., 296115; from *J. Soc. Chem. Ind.*, 1917, **36**, 616).—A mixture of argon, etc., with nitrogen, hydrogen, oxides of carbon, methane, and such gases, is treated in a tube connected with a manometer and a two-way tap, with metallic calcium in the form of large crystals, or with alloys of calcium with magnesium and aluminium, and with calcium nitride. The former absorbs all nitrogen and the latter hydrogen, methane, etc., at temperatures between 200° and 650°. H. W.

Estimation of Potassium. The Lindo-Gladding Method. P. L. Hibbard (*J. Ind. Eng. Chem.*, 1917, **9**, 504—513).—A study was made of the Lindo-Gladding method for the estimation of potassium, particularly from an agricultural chemical point of view, and the following are the more important observations made. The solution is preferably made by extraction with hot water on a tube filter. The volume of water used, the excess of ammonia, and time of keeping before filtering are immaterial. The ammonia should be added before the ammonium oxalate, and if there is more than enough phosphate present to precipitate the bases, the oxalate should not be used at all, unless, as when a great excess of soluble phosphate is present, calcium chloride is previously added in slight excess to precipitate this. Occlusion of potassium salts in the gelatinous calcium phosphate must be guarded against either by reprecipitation or by greater dilution of the original solution. In igniting the salts with sulphuric acid, the temperature must be kept below the fusion point until all the carbon is burned off. The residue is dissolved in dilute hydrochloric acid, the silica filtered off, and the solution diluted to such an extent that on the addition of platinic chloride no immediate precipitation occurs. The solution is then evaporated until it is pasty, but not dry; it should be kept just acid with hydrochloric acid, and excess of platinic chloride should be avoided if much sodium is present. The purification of the potassium platinichloride is usually completed by five or six washings with 10 c.c. of 80% alcohol, and it is best collected in an ordinary Gooch crucible and dried for an hour at 120°. The perchlorate method for the estimation of potassium is longer, more difficult, and more expensive than the platinum method.

G. F. M.

Estimation of Potassium and Sodium in the Form of Sulphates by Platinum Chloride. (MLLE.) BRONISLAVA TURKUS (*Ann. Chim. anal.*, 1917, **22**, 101—102).—The mixed sodium and potassium sulphates are weighed and dissolved in water, and to the solution the calculated quantity of platinum chloride and a little hydrochloric acid are added in small portions, the solution being evaporated to dryness between each addition. The sodium platinichloride is removed by washing the precipitate with 85% alcohol, and the potassium platinichloride dried and calcined. The residual platinum is washed, dried, ignited, and weighed. The sodium is estimated by difference. W. G.

Estimation of Sodium Sulphide in Sulphide Dyebaths. H. SWANN (*J. Soc. Dyers*, 1917, **33**, 146—148).—A rapid method based on the conversion of sodium sulphide into ammonium sulphide, and the distillation of this into a known volume of standard iodine solution acidified with acetic acid.

Fifty c.c. of the dye liquor are diluted to 250 c.c., and 20 c.c. of this liquid are transferred to a conical flask. To this liquid 10—20 c.c. of a 25% solution of ammonium chloride are added, and the mixture is distilled for not more than five minutes into 25 c.c. of *N*/10-iodine solution diluted with 100 c.c. of water and acidified with acetic acid. The excess of iodine is titrated with *N*/10-thiosulphate solution, using starch as an indicator. One c.c. of *N*/10-iodine solution = 0·012 gram of sodium sulphide, $Na_2S,9H_2O$. Thiosulphates, carbonates, and sulphates have no influence on the estimation. In the presence of sulphide dyestuffs, results are obtained varying with the amount of dyestuff present. In the presence of sulphite, results were obtained varying with the amount of sulphite present, owing to a reaction which was not further investigated. W. G.

Estimation of the Alkalinity and Phosphoric Acid Content of the Ash of Feeding Stuffs. I. M. Kolthoff (*Chem. Weekblad*, 1917, **14**, 547—558. Compare A., 1916, ii, 538; Pfyl, A., 1914, ii, 290).—The author does not consider that Pfyl's method for estimating the alkalinity of the ash of foods possesses any advantage over his own. A. J. W.

New Applications of Thymolphthalein and Naphtholphthalein in the Estimation of True Neutrality in Waters, including Rapid Methods for Analysing Limestone and Ammonium Salts. J. Moir (*J. Chem. Met. and Min. Soc. S. Africa*, 1917, **17**, 129—132; from *J. Soc. Chem. Ind.*, 1917, **36**, 571). —The insensitiveness of thymolphthalein to traces of alkali, particularly in boiling solutions, has been utilised in the estimation of lime and magnesia in limestone; 0·5—0·75 gram of the sample, free from grit, is mixed with about 10 c.c. of 2*N*-hydrochloric acid, the mixture heated on the water-bath for about twenty minutes, the turbid liquid diluted to about 20 c.c., and titrated with *N*/2-sodium hydroxide solution (free from carbonate), using a methyl-red solution (0·02%) in dilute alcohol as indicator; the combined acid equivalent of the lime and magnesia is thus obtained. After diluting to 50 c.c. and boiling for one minute, 3 c.c. of 1% thymolphthalein solution in 60—70% alcohol, and then sufficient *N*/2-sodium hydroxide to give a dark blue solution, are added, the mixture boiled for one minute to coagulate the precipitated magnesia, and the blue suspension titrated until yellow with *N*/2-hydrochloric acid; in this manner, the magnesia content is determined, and the lime may be obtained by difference. A correction should be made if an appreciable amount of phosphate is present. The results agree closely with those obtained by the ordinary method.

In analysing the ammonium salts of strong acids, the solution, previously neutralised to methyl-red if necessary, is titrated at the boiling point with *N*/5-sodium hydroxide in presence of a small quantity of a saturated solution of thymolphthalein in 50% alcohol until the deep blue to green colour reappears and withstands boiling for twenty seconds.

The true neutrality of water is estimated by using as mixed indicators methyl-red and α-naphtholphthalein, which are much more sensitive than methyl-orange and phenolphthalein, and will detect 0·1 part of sulphuric acid and 0·2 part of calcium hydroxide per 100,000. In the presence of more than 0·4 part of acid in 100,000, the colour is violet-rose; 0·2 part of acid, salmon-orange; neutral, straw-yellow; 0·2 part of alkali, citrine-green; more than 0·4 part of alkali deep bluish-green. Neutral red, rosolic acid, or alizarin may be used in place of methyl-red. H. W.

Microchemistry of Plants. V. Detection of Dissolved Calcium Compounds by means of Sodium Carbonate. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1916, **34**, 288—295).—One of the most sensitive reactions for the microchemical detection of calcium in plant tissue consists in treatment with concentrated aqueous sodium carbonate solution (from 10% to an almost saturated solution), which results in the precipitation of sodium calcium carbonate or gaylussite crystals. The rapidity and abundance with which the crystals are formed increase with the concentration of the sodium carbonate solution employed.

T. H. P.

Microchemistry of Plants. VI. Detection of Lime by means of Potassium Hydroxide or a Mixture of Potassium Hydroxide and Carbonate. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1916, **34**, 357—363).—Treatment of a plant section containing dissolved or undissolved calcium compounds with a drop of semi-saturated aqueous potassium hydroxide leads to the gradual formation of characteristic, hexagonal plates or disks, which may change later into crystalline aggregates resembling full-blown flowers. The crystals consist of the double salt,

$$2CaCO_3,3K_2CO_3,6H_2O.$$

This test is rendered more rapid and certain if the semi-saturated potassium hydroxide solution (1 vol.) is mixed with saturated potassium carbonate solution (1 vol.). The reaction takes place with calcium carbonate, sulphate, nitrate, phosphate, oxalate, malate, tartrate, acetate, or butyrate.

T. H. P.

Properties of Barium Sulphate. Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1917, **56**, 225—246).—Pure barium sulphate may be obtained from the product contaminated with barium chloride by dissolving it in concentrated sulphuric acid, heating the solution for a long time, precipitating the barium sulphate by diluting with much water, and washing and drying the precipitate. Such barium sulphate does not lose in weight when heated over a Teclu burner in either a platinum or a porcelain crucible. When heated for an hour in a blowpipe flame, it is, however, diminished appreciably in weight, especially in a platinum crucible, and the resultant salt smells of hydrogen sulphide in the cold. The barium sulphide thus formed undergoes very slow oxidation when heated over a Teclu burner. In a porcelain, but not in a platinum, crucible, diminution in weight (for instance, from 1·0622 to 1·0608 gram) occurs when barium sulphate is ignited in contact with filter paper; the amount of the loss is inconstant and small, but in accurate work the dried precipitate should be separated from the filter paper and the latter burnt in another crucible.

Direct determinations have been made of the solubility of barium sulphate in water and in solutions of various acids and salts by boiling a known weight of the pure salt for two hours with 200 c.c. of a solution of the electrolyte, allowing to remain with frequent shaking for twenty-four hours, filtering, washing with 350 c.c. of water, igniting, and weighing; the amount of barium sulphate dissolved in the washing water was determined separately and the results corrected accordingly. The solubility per litre is 0·0043 gram in pure water, or 1 in 232,558; that this solubility is considerably higher than that previously found by other investigators (1 in about 400,000) is explained by the fact that the salt used is of very fine grain and passes even through a double filter. Barium sulphate occludes barium chloride in amount depending on the concentration of the chloride, such occlusion depending on the fineness of the precipitate. The solubility of barium sulphate in sulphuric acid solutions is actually diminished or even destroyed if the concentration of the acid is higher than 0·3*N*; with lower concentrations, the solubility is almost the same as in pure water.

The solubility of barium sulphate in solutions of potassium chloride or nitrate is greater than in water, owing to double decomposition between the barium sulphate and the potassium salt; it is thus evident that, under these conditions, the barium and sulphate radicles exist in solution, not only in the ionic state, but also partly as undissociated barium chloride, barium nitrate, and potassium sulphate molecules. Potassium sulphate or a mixture of either potassium chloride and sulphate or potassium chloride and sulphuric acid also increases, but only slightly, the solubility of barium sulphate in water. Towards sodium sulphate or a mixture either of sodium chloride and potassium sulphate or of sodium chloride and sulphate, barium sulphate behaves in the same way as towards the corresponding potassium salts. Sodium chloride increases the solubility, but not with similar dependency on the concentration as with potassium chloride, and the results are not reproducible.

In 1·44*N*-calcium chloride, the weight of barium sulphate found is greater than that taken, but at lower concentrations the weight diminishes; the amount of the diminution does not, however, depend on the concentration of the calcium chloride, but is equal to the solubility of the barium sulphate in pure water. The solubility of barium sulphate, or, more accurately, its diminution in weight, is greater than in water or calcium chloride solutions; strontium chloride behaves, however, quite differently from calcium chloride, owing to the comparatively slight solubility of strontium sulphate and the consequent diminished formation of sulphate ions.

In 0·118*N*-lead nitrate solution, barium sulphate increases in weight, owing to interaction of the two salts, and consequent precipitation of lead sulphate. With lower concentrations of the lead ion, the amount of lead sulphate formed diminishes, and so also does the weight of the precipitate, a minimum being reached which corresponds with the solubility of the barium sulphate under the experimental conditions; finally, the solubility in pure water is attained.

Barium sulphate is insoluble in ferric sulphate containing sulphuric acid, and sometimes increases slightly in weight, owing to adsorption by the precipitate and filter paper. In ferric chloride solution containing hydrochloric acid, barium sulphate exhibits marked solubility, which depends on the concentration of the ferric salt; in ferric chloride solution containing barium chloride, barium sulphate is, however, insoluble. In hydrochloric acid solutions the solubility is considerably greater than in solutions of potassium, sodium, or strontium chloride, etc., and is also greater, though not so much so, than in ferric chloride solutions; the solubility depends, indeed, solely on the concentration of the hydrogen ion. In nitric acid, barium sulphate is more soluble than in hydrochloric acid, ferric chloride, etc., but if barium chloride or sulphuric acid is also present, the precipitate is practically insoluble in nitric acid.

The solubility of barium sulphate in different electrolytes is determined by two factors, the anion and the cation. The anion, SO_4'', diminishes the solubility, NO_3' increases it, and Cl' is indifferent. Of the cations, $Ba^{\cdot\cdot}$ diminishes the solubility of barium sulphate, whilst $Ca^{\cdot\cdot}$ is indifferent, and $K^{\cdot}$, $Na^{\cdot}$, $Sr^{\cdot\cdot}$, $Pb^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, and $H^{\cdot}$ increase it. T. H. P.

The Analysis of Zinc Alloys. MOSSBACHER (*Zeitsch. öffentl. Chem.*, 1917, **23**, 113—115).—Details are given of a rapid method for the full analysis of zinc alloys. After dissolving in concentrated nitric acid and evaporating to one-third bulk, sulphuric acid is dropped into the middle of the liquid, and heating is continued until white fumes are evolved. Water and alcohol are added, and after several hours the lead sulphate is collected. The filtrate is ignited in a crucible which has just previously been heated with a drop of sulphuric acid. Copper is precipitated as sulphide and heated with sulphur in hydrogen in a silica crucible. Aluminium and iron are precipitated from the filtrate, after removal of hydrogen sulphide, by adding hydrogen peroxide, and then, rapidly, a large excess of ammonia. By adding a little Congo-red, that part of the colloidal precipitate which always adheres to the glass is made clearly visible.

Iron is estimated volumetrically in a separate portion.

C. H. D.

Estimation of Manganese in Iron and Steel according to the Bismuth Method. H. KINDER [*Chemikerkommission des Vereins deutscher Eisenhüttenleute*] (*Stahl u. Eisen*, **37**, 197—202; from *Chem. Zentr.*, 1917, i, 817—818).—In continuation of previous work on the estimation of manganese by the permanganate (*Stahl u. Eisen*, 1913, **33**, 633) and chlorate or persulphate (*ibid.*, 1915, **35**, 918) methods, the commission has examined the data concerning the bismuth process, using sodium bismuthate or bismuth tetroxide. The original memoir must be consulted for details. The method, however, is not suited for purposes of investigation, and cannot be recommended for the works laboratory because of its complicated nature and the necessity of keeping the temperature below 25° (increase of temperature causes low results for Mn). The Volhard-Wolff permanganate method is suitable for investigation, and can be used in the examination of ores, raw iron, steel, and ferromanganese. It can be employed equally well in hydrochloric or nitric acid solution, but sulphuric acid solutions are to be avoided. The presence of chromium is immaterial if the precipitated zinc oxide is removed; molybdenum and vanadium are without influence, but cobalt, which is usually only present in small amount, causes high results. The chlorate process can only be employed in nitric acid solution, and is particularly suitable for iron and steel; it is less accurate for estimating small amounts of manganese and for ferromanganese. Considerable quantities of chromium cause slightly high results. The persulphate process is adapted to works practice because of its rapidity. The presence of considerable quantities of chromium or cobalt makes the end-point difficult to detect on account of the yellow or pink colorations which they impart to the solutions.

H. W.

Evaluation of Pyrolusite. E. Rupp (*Arch. Pharm.*, 1916, **254**, 135—137).—To 0·2 gram of very finely powdered pyrolusite are added 3 grams of potassium iodide, 3 grams of sodium phosphate, 10 c.c. of water, and 10 c.c. of officinal (25%) phosphoric acid. The mixture is well shaken for one minute, and kept for thirty to sixty minutes with occasional shaking; about 50 c.c. of water are then added, and the liberated iodine is titrated with *N*/10-thiosulphate with starch as indicator. A reappearance of the blue coloration indicates that the pyrolusite has not been sufficiently finely ground.

C. S.

Differential Iodometry. IV. The Analysis of Pyrolusite and other Oxidised Manganese Ores. O. L. Barnebey and Geo. M. Bishop (*J. Amer. Chem. Soc.*, 1917, **39**, 1235—1238. Compare this vol., ii, 274).—In a previous paper a method was described for the estimation of the available oxygen in pyrolusite and other higher oxides of manganese (*loc. cit.*). This method, however, is untrustworthy if appreciable amounts of ferric iron are present. The present paper gives an account of a method which may be used for pyrolusite containing large amounts of iron. The method depends on two principles: (1) When finely divided pyrolusite is treated with hydrochloric acid and potassium iodide, iodine is liberated; iodine is also liberated by ferric chloride in acid solution. (2) When neutral ferrous chloride is brought into contact with excess of iodine, it is instantaneously oxidised to the ferric condition. The following is the method recommended. A sample of the finely powdered ore (0·2 gram) is placed in a 300 c.c. flask and treated with 10 c.c. of *N*-sodium iodide and 5 c.c. of concentrated hydrochloric acid. The flask is repeatedly shaken until the reaction is complete; 0·2—0·5 gram of powdered sodium tartrate is then added, and the solution diluted to 150 c.c. Sodium hydrogen carbonate is added in excess and the free iodine titrated with arsenite. The addition of tartrate is to prevent hydrolysis of the ferric salts on dilution. The results agree well with those obtained by other methods. J. F. S.

Iron Oxide as Standard in the Volumetric Estimation of Iron in Hydrochloric Acid Solution. H. KINDER (*Stahl u. Eisen*, **37**, 266; from *Chem. Zentr.*, 1917, i, 817).—A discussion of the proposal of Brandt (A., 1916, ii, 539) to use pure iron oxide, prepared from ferrous oxalate, as standard. H. W.

Ammonio-cobalt Molybdate, Tungstate, and Vanadate. Estimation and Separation of Cobalt. ADOLPHE CARNOT (*Compt. rend.*, 1917, **164**, 897—903.* Compare A., 1889, 1116, 1117).—The cobaltous chloride is converted into roseo- or purpureocobalt chloride by means of hydrogen peroxide in the presence of ammonium chloride and ammonia, and the solution is just neutralised with hydrochloric or acetic acids. To the cold, dilute solution just sufficient of a 5% aqueous solution of ammonium molybdate is added. The pink precipitate is dried at 110° and weighed. It has the composition $Co_2O_3,10NH_3,6MoO_3$. If this precipitate is ignited, the ammonia is driven off, and at the same time the cobalt sesquioxide and the molybdic anhydride are partly reduced. If ammonium tungstate is used instead of the molybdate, the precipitate obtained, when dried at 110°, has the composition $Co_2O_3,10NH_3,6WO_3,xH_2O$. With ammonium vanadate a pink precipitate is first obtained having the composition $Co_2O_3,10NH_3,3V_2O_5$, but with an excess of the vanadate solution a yellow precipitate is obtained having the composition $Co_2O_3,10NH_3,6V_2O_5$. It is most satisfactory for quantitative work to weigh the cobalt as the double molybdate. This method can be used for the estimation of cobalt in the presence of nickel, provided that the estimation is carried out rapidly and the precipitate is well washed with water. If the nickel is in excess, it is advisable to redissolve the precipitate in ammonia and reprecipitate it by neutralisation with acid and the addition of a little ammonium molybdate. Any iron and manganese present in the original solution will be precipitated by the ammonium hydroxide and hydrogen peroxide. In the presence of zinc, cadmium, or copper, it is advisable to dissolve and reprecipitate the double molybdate twice. W. G.

α-Benzildioxime [Reagent for Nickel]. HERMANN GROSSMANN and JULIE MANNHEIM (*Ber.*, 1917, **50**, 708—711).—The authors have tested Atack's method for detecting and estimating nickel in which α-benzildioxime is the precipitant (A., 1913, ii, 730). The reagent is best prepared by warming a methyl-alcoholic solution of benzil with powdered hydroxylamine hydrochloride and a few drops of hydrochloric acid, the oxime being filtered off from time to time. It is applied in the form of a saturated, alcoholic solution. For the separation of nickel from zinc or magnesium, ammonium chloride is added; manganese is retained in solution by means of citric acid and hydrazine (to prevent oxidation);

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* and *Ann. Chim. anal.*, 1917, **22**, 121—126.

copper is kept in solution by means of Rochelle salt, but only small proportions should be present. The nickel precipitate does not suffer loss of weight even at 180°. J. C. W.

Analysis of Cast Nichrome. E. W. Reid (*J. Ind. Eng. Chem.*, 1917, **9**, 488—490).—A detailed description is given of a scheme for the complete analysis of nickel–iron–chromium alloys. The alloy is first dissolved in nitrohydrochloric acid, and the silicon volatilised from the residue by treatment with hydrofluoric acid. The small residue of metal initially enclosed by the silica is now dissolved by a second treatment with nitrohydrochloric acid after fusion, if necessary, with sodium peroxide. In fractions of the 'stock' solution of the alloy thus obtained, the metals are estimated in the order given: (*a*) nickel by the cyanide method; (*b*) iron and chromium by precipitation as hydroxides and oxidation to ferric hydroxide and chromate respectively with bromine water; (*c*) manganese by precipitation with potassium chlorate in presence of nitric acid and titration of the precipitate with ferrous ammonium sulphate, zinc in the filtrate from the iron and chromium estimation after removal of the nickel by means of dimethylglyoxime, by titration with potassium ferrocyanide, and, finally, carbon by direct combustion in oxygen. G. F. M.

Estimation of Chromium in Ferrochrome. P. Koch (*Stahl u. Eisen*, **37**, 266; from *Chem. Zentr.*, 1917, i, 817. Compare this vol., ii, 337).—In contrast to Schumacher (this vol., ii, 337), the author maintains the correctness of the factor 0·3109 by which the iron titre must be multiplied to obtain the chromium titre. H. W.

Separation of Antimony and Tin by Hydrogen Sulphide in Hydrochloric Acid Solution, and their Iodometric Estimation. Aug. Prim (*Chem. Zeit.*, 1917, **41**, 414—415).—Antimony and tin (stannous) can be completely separated by means of hydrogen sulphide if the solution contains a certain amount of hydrochloric acid. Preliminary tests with pure materials show that the best conditions are when the volume of liquid is 200 c.c. and the amount of hydrogen chloride present 26·58 grams (60 c.c. of acid of D 1·19). The antimony sulphide may be dissolved in concentrated hydrochloric acid and estimated iodometrically in the usual way after boiling away the hydrogen sulphide. The filtrate containing stannous chloride may also be boiled to remove hydrogen sulphide, with the addition of ferrum reductum, and finally titrated with iodine.

The application of the process to the analysis of alloys will be described later. J. C. W.

Detection of Methyl Alcohol by Catalytic Dehydrogenation. C. Mannich and W. Geilmann (*Arch. Pharm.*, 1916, **254**, 50—64).—The method consists in passing the vapour of the liquid under examination over pumice impregnated with reduced copper at 280—300°. The course of the decomposition has been already described (A., 1916, i, 362). The formaldehyde produced is detected by the violet coloration it develops with morphine and concentrated sulphuric acid. The apparatus is figured and described. An aqueous solution containing 0·1% of methyl alcohol gives a condensate which develops the coloration very faintly after one hour and faintly after twenty-four hours. The method is very effective in detecting methyl alcohol in blood or urine, 0·01 gram of the alcohol in 100 c.c. of blood or urine giving a positive result; the liquid must first be carefully fractionated to concentrate the methyl alcohol, and the fraction containing the latter must be boiled for some time with freshly ignited animal charcoal before being passed over the catalyst, although even with these precautions the catalyst is slowly poisoned.

In order to detect methyl alcohol in the presence of ethyl alcohol, the mixture, diluted if necessary so that it contains about 50% of water, is passed over the catalyst, the condensate is heated in a vacuum to remove the acetaldehyde, and the residual solution is tested for formaldehyde as above. If the original mixture contains less than 1% of methyl alcohol, the diluted solution should be repeatedly fractionated before the test is applied to the fraction in which the methyl alcohol has been concentrated. One-half per cent. of methyl alcohol in brandy can be detected by this method. C. S.

Estimation of Alcohol and Water in Ether for Anæsthesia. R. L. Perkins (*J. Ind. Eng. Chem.*, 1917, **9**, 521—523).—The method differs from that of Mallinckrodt and Alt (A., 1916, ii, 583) in that the water is estimated from the specific gravity of the original mixture, and for this purpose specific gravities of ether–alcohol–water mixtures were determined to the fifth place of decimals, and the results are presented in the form of a curve, specific gravities being plotted against percentages of alcohol for varying proportions of water up to 1%. The specific gravities of the original ether and of the sample after drying for twenty-four hours over potassium carbonate are determined at 25°, and percentages of alcohol and water can then be read off directly from the above-mentioned curve. G. F. M.

Solubility of Cholesterol-digitonide. J. Howard Mueller (*J. Biol. Chem.*, 1917, **30**, 39—40. Compare Bloor and Knudson, A., 1916, ii, 650).—Bloor contends that the low figures obtained in the estimation of cholesterol by gravimetric as compared with colorimetric methods are due to losses incurred in the washing of the cholesterol–digitonide with ether and hot water. The author finds, however, that the solubility of the pure digitonide in either of these solvents is so slight that any error arising from this cause would not account for more than 10% of the discrepancy actually observed. H. W. B.

Estimation of Dextrose in Urine. G. Frerichs and E. Mannheim (*Arch. Pharm.*, 1916, **254**, 138—148).—The authors prefer Rupp and Lehmann's iodometric method of estimating reducing sugars to the Fehling-Soxhlet method, and deny Ruoss's statement (A., 1916, ii, 155) that the iodometric estimation of the excess of the cupric salt remaining after Fehling's solution has been partly reduced by a sugar solution yields untrustworthy results, owing to the action of oxidised sugar compounds on the liberated iodine. They find that the substances produced from the sugar by the action of the alkaline copper solution have no action on iodine. The table published by Rupp and Lehmann giving the number of mg. of dextrose corresponding with a given consumption of $N/10$-thiosulphate has been incorrectly calculated, and the authors give a list of corrected values.

In estimating the sugar in urine, Rupp and Lehmann add 20 c.c. of the urine, diluted if necessary so that not more than 0·5% of dextrose is present, to a definite quantity of the Fehling's solution under definite conditions. In preference to this, the authors adopt the following quantities, since the use of tables is thereby avoided and the calculation of the result is greatly simplified. They have observed from the figures given in the table that when the number of mg. of dextrose is divided by the number of c.c. of $N/10$-thiosulphate, the quotients vary from 3·23 to 3·42. Taking the mean value (1 c.c. of $N/10$-thiosulphate is equivalent to 3·33 mg. of dextrose), the error in the calculation is in the most unfavourable cases only about one-thirtieth of the amount of sugar present. The authors therefore use for the estimation 3·33 c.c. of urine (readily measured by diluting 10 c.c. of the urine with 20 c.c. of water and taking 10 c.c. of the mixture) and 15 c.c. of the copper sulphate solution (70 grams of hydrated copper sulphate dissolved and made up to 1 litre); with these quantities, the percentage amount of dextrose (that is, the mg. of dextrose in 100 c.c. of urine) is almost exactly equal to one-tenth of the number of c.c. of $N/10$-thiosulphate representing the difference between the volume of thiosulphate required in standardising 15 c.c. of the copper sulphate solution and that used in titrating the excess of copper sulphate in the estimation. When the urine contains less than 1% of dextrose, 10 c.c. of undiluted urine should be used, and for less than 0·5% of dextrose 20 c.c. of undiluted urine, the percentage of dextrose being then obtained by dividing the above difference by 30 and by 60 respectively. When more than 3·5% of dextrose is present, one-half of 3·33 c.c. of urine should be used, the above difference being multiplied by 5 to give the percentage of dextrose.

The original should be consulted for a detailed description of the method of procedure. When 10 or 20 c.c. of undiluted urine are used, the iodine value (in c.c. of $N/10$-iodine) of this quantity must be estimated and subtracted from the difference mentioned above. C. S.

Estimation of Small Amounts of Sugar in the Urine. ALMA HILLER (*J. Biol. Chem.*, 1917, **30**, 125—127).—In this method, the creatinine and reducing substances other than dextrose are first removed from the urine by treatment with animal charcoal and picric acid (Folin, A., 1915, ii, 802), and the dextrose in the filtrate is then estimated by Lewis and Benedict's method (A., 1915, ii, 111). H. W. B.

A New Method for the Estimation of Aldoses. J. Bougault (*Compt. rend.*, 1917, **164**, 1008—1011).—The method is based on the reaction $R{\cdot}CHO + H_2O + 2I = R{\cdot}CO_2H + 2HI$, which is, however, not instantaneous, the velocity depending on the excess of iodine used. The sugar, in aqueous solution, is heated with about three times the theoretical amount of iodine and a 15% solution of crystalline sodium carbonate. The oxidation is complete at the end of thirty minutes, after which the excess of iodine is titrated with sodium hyposulphite solution. The method was found to be applicable to all the aldoses tried, except that in the case of mannose the mixture had to be boiled for ninety minutes. The author has studied the action of iodine and sodium carbonate on the ketoses and the non-reducing sugars, and the influence of alkalinity, temperature, and light on the velocity of oxidation, and the estimation of aldoses in the presence of ketoses and non-reducing sugars. In all cases there is a slight secondary reaction, which can be allowed for by determining the amount of iodine absorbed during a further thirty minutes' heating. The ketoses and the non-reducing sugars are not appreciably oxidised by the reagent, and thus do not interfere with the estimation of aldoses unless they are present in excessive amounts.
W. G.

Simplified Inversion Process for the Estimation of Sucrose by Double Polarisation. Herbert S. Walker (*J. Ind. Eng. Chem.*, 1917, **9**, 490—492).—Certain of the difficulties encountered in the inversion of sucrose in the Herzfeld-Clerget method of estimation by double polarisation are obviated by the following method of procedure, which is specially recommended for technical practice. The solution used for direct polarisation is placed in a 100 c.c. flask and heated on a water-bath at 65—67°; it is then removed from the bath, 10 c.c. of diluted hydrochloric acid (1:1) are added, and the whole allowed to cool spontaneously in air. After fifteen minutes inversion is complete, and the solution, made up to 100 c.c., is ready for polarisation. In the case of products which have been clarified with basic lead acetate, the excess alkalinity must be destroyed before heating on the water-bath by adding 1 to 2 c.c. of the above diluted hydrochloric acid, otherwise serious losses occur. Errors due to destruction of lævulose are by this method of inversion largely eliminated, and the rigid adherence to specified temperatures and duration of heating required by the Herzfeld method is unnecessary, a latitude of 10° in temperature causing no appreciable inaccuracy in results. G. F. M.

Biological Examination of Honey. J. Gadamer [with Karl Laske] (*Arch. Pharm.*, 1916, **254**, 306—345).—One of the most difficult tasks of the food analyst is to prove the genuineness of bee-honey by chemical analysis, especially since solutions of very pure invert-sugar with or without raffinose, which can be used to adulterate natural honey or to prepare artificial honey, have become easily obtainable. Fiehe's reaction, which detects hydroxymethylfurfuraldehyde in technical invert-sugar, is not conclusive, and methods based on the estimation of the nitrogen and albumin in natural honey are easily evaded.

The precipitin reactions of Kraus (A., 1904, ii, 423), Wassermann, and Uhlenhuth could be usefully employed in the examination of honey provided the proteins occurring in the honey originate in the bee's body and not in the plant from the nectaries of which the bee collects the material of which the honey is made. In 1902 von Rigler prepared an anti-serum specific for genuine honey, and in the same year Langer obtained a serum which gave a copious precipitate with buck-wheat honey. The researches of the latter investigator show that the honey albumin is quite independent of the plant visited by the bee.

An important advance was made by Thöni (*Veroffl. Schweiz. Ges.-amt*, 1911, **2**, 80; 1912, **3**, 74), who placed the precipitin method on a more or less quantitative basis and ascertained the amount of precipitate normally given by a genuine unheated bee-honey under definite experimental conditions. Since Klostermann (*Jahrsb. Hyg. Inst. Halle*, 1909) has reported less favourably on the precipitin method, the authors have reinvestigated the subject. In order to obtain the antigens, a sample of genuine honey (75 grams) was dialysed for forty-eight hours, the sugar-free liquid was shaken with 70% of finely powdered ammonium sulphate, the albumins were collected after two hours, suspended in 10 grams of sterilised, distilled water, and, after the addition of 0·5% of toluene, dialysed for about forty-eight hours to remove the ammonium sulphate. Each dialysis yielded about 20 grams of injection liquid. To obtain the anti-substance, as a preliminary the normal serum of each dog was tested with 2—10% solutions of the honey used to supply the antigens; in no case was a precipitate obtained after five hours. The albumin suspensions, freshly prepared in every case, were introduced (3—6 c.c.) by intraperitoneal injection for several weeks at intervals of a few days, eight to twelve injections being made. Samples of blood were withdrawn at intervals and the anti-sera obtained tested, after filtration through kieselguhr, for their activity and specificity. Suitable anti-sera (0·2—0·5 c.c.) were mixed with 1 c.c. of 1—10% honey solutions, of 10% artificial honey solution, of 10% starch syrup solution, also 0·5 c.c. of normal serum was mixed with 1 c.c. of 10% honey solution; each mixture, after the addition of one drop of toluene, was vigorously shaken and kept at 37° for five hours, the tubes were centrifuged (1500 rev. per minute) for five minutes, and the volume of the precipitate (if any) read off in mm.

The authors have set themselves the questions: (1) does the preservative toluene affect the reaction and is its addition necessary; (2) is the precipitation constantly quantitative, in other words, do two different anti-sera, which yield equal amounts of precipitates with one honey, also give equal amounts with another honey; (3) are the precipitates obtained from 10%, 2%, and 1% honey solutions quantitatively comparable; and (4) does the storing of honey effect any change in its content of specific albumins? They find that: (1) Preservation of the liquid during the time of the experiment is unnecessary. The presence of toluene causes the formation of emulsions and renders a quantitative separation of the precipitate by centrifuging impossible. In the absence of toluene, quantitative results are obtained. (2) An absolute constancy in the activity of the precipitating serum cannot be claimed. Different anti-sera give approximately equal amounts of precipitate, but the variations are not so great as to render the method inapplicable for quantitative purposes. (3) With a given anti-serum, the amounts of precipitate obtained from 2% and 1% solutions of a honey are by no means comparable; therefore, in examining a honey by the biological method, only the values obtained with a 10% solution should be utilised. (4) The amount of precipitate obtained from a given honey and the same anti-serum is the same during the period of one year. A specimen of genuine honey which had been kept for eleven years gave, however, only a very small precipitate.

The authors are of opinion, therefore, that the precipitin reaction has a real quantitative value. All honeys which do not give a precipitate with honey albumin anti-serum are not to be regarded as genuine bee-honeys. If a precipitate is obtained and its amount corresponds with that obtained from the control honey, the honey under examination is genuine. If the amount of the precipitate is smaller than that given by the control, the honey under examination is either genuine honey which has been heated or honey which has been adulterated.

The paper contains numerous tables of results and concludes with a bibliography of the subject. C. S.

Examination of Acetic Anhydride. L. G. RADCLIFFE and F. MEDOFSKI (*J. Soc. Chem. Ind.*, 1917, **36**, 628—630).—The authors have examined various methods of estimating acetic anhydride in the commercial product, and are led to the conclusion that the direct titration process (decomposition of anhydride by water and estimation of the acid by titration with *N*/1-sodium hydroxide) is the shortest, but the British Expert Committee's method (Report on the Analysis of Crude Glycerine, 1911) is the safest, since the results derived from direct titration are controlled by the data obtained by allowing weighed quantities of the anhydride to react with a considerable excess of aniline and estimating the acid formed.

Much of the acetic anhydride now available is yellow, and the coloration is difficult to remove by simple distillation; it may be eliminated by distillation over phosphoric anhydride, but the process causes a slight diminution in the content of acetic anhydride.

According to the authors' experience, crystalline sodium acetate does not effloresce on exposure to air, but can be readily completely dehydrated at 97—100° or by the aid of calcium chloride at the ordinary temperature. The anhydrous substance is very hygroscopic. H. W.

Testing of Acetic Anhydride. C. E. Sage (*Perfumery and Ess. Oil Rec.*, 1917, **8**, 162—163; from *J. Soc. Chem. Ind.*, 1917, **36**, 667—668).—In estimating the value of acetic anhydride, the total acidity is determined by direct titration with alkali hydroxide solution and also the residual acidity after treatment with aniline in the cold, by which the anhydride is decomposed with the production of equimolecular parts of acetanilide and acetic acid. From these two titration numbers, the amount of anhydride is calculated, the remaining acidity being due to acetic acid or to acetic and butyric acids if the latter is present, which is determined by a preliminary qualitative analysis; the relative proportions of these two acids may also be calculated from the same titrations. It is suggested from the figures obtained and the large-scale results when using anhydride containing butyric acid that anhydrides other than acetic may also be present. H. W.

Shaffer's Oxidation Method for the Estimation of β-Hydroxybutyric Acid in Urine. N. O. Engfeldt (*Zeitsch. physiol. Chem.*, 1917, **99**, 166—223).—The author finds that although the oxidation of β-hydroxybutyric acid to acetone by chromic acid is not quantitative, yet Shaffer's method for the estimation of β-hydroxybutyric acid in urine by this means yields satisfactory results provided certain precautions are taken and corrections applied. H. W. B.

Improvements in the Copper Method for Estimating Amino-acids. Philip Adolph Kober (*J. Ind. Eng. Chem.*, 1917, **9**, 501—504).—Certain improvements are described in the technique of the copper method for estimating amino-acids. As an easily prepared iodometric standard, a copper sulphate solution prepared from anhydrous copper sulphate is recommended, and a simple method for its preparation by dehydrating the salt in a test-tube heated in an oil-bath at 250° is described. A stock suspension of cupric hydroxide, which retains its activity for months and obviates the necessity of a fresh preparation every day, is obtained by precipitating with less alkali than is required for the complete precipitation of the copper. To avoid the daily preparation of potassium iodide starch solutions, a saturated solution may be prepared and kept almost indefinitely in a flask under a layer of oil after boiling for thirty minutes to expel oxygen, the neck of the flask being closed with a bung carrying a trap containing strong sodium hydroxide. In conclusion, a summarised description of the complete amino-acid estimation is given.

G. F. M.

Simple Method of Estimating the Contents of Sozoiodol-mercury Preparations. A. Herrmann (*Arch. Pharm.*, 1916, **254**, 498—500. Compare Rupp and Hermann, this vol., i, 488). —The mercury in hydrargyrum sozoiodolicum (mercuric salt of di-iodophenol-*p*-sulphonic acid, $C_6H_2I_2<\substack{O—\\SO_3}>Hg$) is readily estimated as follows. The preparation, 0·5 gram, is shaken with about 10 c.c. of water in a 200-gram glass-stoppered bottle, treated with 2 grams of potassium iodide, and, after the liberated mercuric iodide has dissolved, basified with 10 c.c. of officinal alkali hydroxide solution. A mixture of 3 c.c. of formaldehyde solution and about 10 c.c. of water is added, and the bottle is gently shaken for about one minute. After acidifying with 25 c.c. of dilute acetic acid, 25 c.c. of $N/10$-iodine solution are added, and the excess of the iodine is titrated with $N/10$-thiosulphate after all the mercury has been dissolved (1 c.c. of $N/10$-iodine = 0·01003 gram of mercury = 0·031225 gram of the mercuric salt).

The mercury in anogon (the mercurous salt, $OHg\cdot C_6H_2I_2\cdot SO_3Hg$) is estimated by treating 0·5 gram with 2 grams of potassium iodide and 25 c.c. of $N/10$-iodine, shaking the mixture for one to three minutes, and titrating the excess of iodine with $N/10$-thiosulphate and starch solution (1 c.c. of $N/10$-iodine = 0·02006 gram of mercury = 0·041256 gram of the mercurous salt). C. S.

The Examination of Oils used in Soap-making. Raoul Lecoq (*Bull. Soc. chim.*, 1917, [iv], **21**, 101—103).—A brief account of a general method stated to be capable of giving good results with all oils. A small quantity of soap is prepared from the oil by alcoholic saponification. Ten grams of this are dissolved in 50 c.c. of water and emulsified with 100 grams of the oil. The mixture is heated on a water-bath, and to it is added, in five successive portions at half-hour intervals, the calculated quantity of sodium hydroxide dissolved in 60 c.c. of water. The mixture is heated for one and a-half hours. The soap is separated, dissolved in 400 c.c. of water, and precipitated by the addition of 125 grams of salt. The soap thus obtained is decanted and washed at the pump, and when cold is examined. W. G.

Estimation of Acetone Substances in the Urine. Emil Lenk (*Biochem. Zeitsch.*, 1916, **78**, 224—230).—The method employed was an iodometric one, in which the substances acting on iodine were first destroyed by treatment with permanganate, and the acetone substances were then directly estimated in the urine without distillation. It was found that the preformed acetone could be estimated by heating the urine with permanganate and acetic acid, in which case the acetoacetic acid is not converted into acetone. After destruction of excess of permanganate with oxalic acid, and precipitation of the manganese hydroxide with sodium hydroxide, the iodometric estimation is carried out in the usual way. To estimate the combined acetone and acetoacetic acid, the urine is first heated with oxalic acid, by means of which the acetoacetic acid is converted into acetone. The total acetone is then estimated by the method above described (boiling with permanganate in solution acidified by acetic acid, etc.). Accurate results can be obtained when only 1 c.c. of urine is employed for the analysis. S. B. S.

Evaluation of Podophyllin. HEINRICH TANZEN (*Arch. Pharm.*, 1916, **254**, 44—49).—The paper gives an account of the extraction of podophyllin from the rhizomes of *Podophyllum peltatum*, Linné, and of the properties of its known constituents, makes a brief comparison between the American and the Indian varieties, and discusses the methods of Jenkins, Gordin and Merrel, Umney, Kremel, and the Dutch pharmacopœia for the estimation of the podophyllotoxin contained therein. The first three methods are condemned on account of the large amount of material required. The last method is recommended. C. S.

Iodine as a Useful Microchemical Reagent for Tannin, especially as regards the Distribution of Tannin and Starch in Vegetable Tissues. ADOLF SPERLICH (*Ber. Deut. bot. Ges.*, 1917, **35**, 69—73).—Iodine in traces may penetrate into cells without injury to the living plasma, the tannins dissolved in the cell-sap gradually forming resistant, characteristic substances of different shades of brown. The substances formed are probably oxidation products allied to or identical with phlobaphens. Other substances, such as oils, resins, etc., also fix iodine, which is removable more or less easily and rapidly by alcohol of various concentrations. The compounds formed in the above way by tannins are highly stable, and the sections may be subjected to further staining operations. T. H. P.

Colorimetric Estimation of Serum-Albumin and Globulin in Urine, Ascitic Fluid, and Blood Serum. W. AUTENRIETH (*Munch. med. Woch.*, 1917, **64**, 241—245; from *Chem. Zentr.*, 1917, i, 699. Compare A., 1916, ii, 163).—The two proteins are estimated together, the method being based on the biuret reaction; the colorations obtained are observed in the Autenrieth–Koenigsberger colorimeter, which is provided with a special "albumin" scale. W. P. S.

Micro-titration with Formaldehyde and its Applications in Physiology. III. Detection of Arginase. A. CLEMENTI (*Atti R. Accad. Lincei*, 1917, [v], **26**, i, 261—264).—Micro-titration with formaldehyde (A., 1915, i, 1025) may be applied to the author's titrimetric method for the investigation of arginase (A., 1915, i, 912), 0·5 c.c. of an arginine sulphate solution containing 0·8% of the base being sufficient to show the action of the enzyme. Arginase is found in the liver of the human embryo, but not in that of the reptile, *Zamenensis Viridiflavus*. T. H. P.

General and Physical Chemistry.

The Distinction between Methylated Nitroanilines and their Nitrosoamines by means of Refractometric Determinations. J. D. JANSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1098—1100).—The following molecular refractivities are recorded: 3:4-dinitrodimethylaniline, 62·8; 3:6-dinitrodimethylaniline, 56·8; 3:4-dinitrodiethylaniline, 73·1; 3:6-dinitrodiethylaniline, 65·3; 3:4-dinitrophenylmethylnitrosoamine, 55·2; 3:6-dinitrophenylmethylnitrosoamine, 52·8; 3:4-dinitrophenylethylnitrosoamine, 59·6; 3:6-dinitrophenylethylnitrosoamine, 57·2.

The difference between the molecular refractivities of the isomeric nitrosoamines is much smaller than that for the corresponding dialkyl compounds. It is also pointed out that the specific refractions of the dinitrodialkylanilines are much greater than the corresponding values for the nitrosoamines. It is suggested that this may be conveniently utilised as a means of distinguishing between the two groups of substances. H. M. D.

The Effect of an Electric Field on the Spectrum Lines of Hydrogen. TOSHIO TAKAMINE and USABURO YOSHIDA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 137—146).—The method of Lo Surdo (*Atti R. Accad. Lincei*, 1913, [v], **22**, 664) has been employed in the further investigation of the influence of an electric field on the hydrogen lines. In this method the spectrum of the glow in the region of discharge immediately in front of the cathode is submitted to investigation, the potential gradient in this region being very large.

The most satisfactory results were obtained with the H_γ line, for which, in addition to the two outer parallel and three perpendicular components, the authors' photographs reveal the existence of four inner parallel components and two inner perpendicular components. These have been identified with components which Stark's method of observation has already shown to occur in the electrically resolved spectrum.

The separation of the inner component lines is found to be proportional to the intensity of the electric field. H. M. D.

The Triplet Series of Radium. GLADYS A. ANSLOW and JANET T. HOWELL (*Proc. Nat. Acad. Sci.*, 1917, **3**, 409—412).—The elements of the second group of the periodic table are characterised by the fact that the principal, first, and second subordinate series of spectral lines contain doublet and triplet series. If the logarithms of the frequency differences between the extreme members of the triplets are plotted against the logarithms of the atomic numbers of the corresponding elements, it is found that alternate elements fall on straight lines. The straight line passing through calcium, strontium, barium, and radium indicates that the frequency difference for the radium triplets should be approximately 3060.

The known radium lines give triplets with average frequency differences of 2016·64, 1036·15, and 3052·79, and it would seem that the last frequency difference is characteristic of the radium spectrum. The first line of the triplet combinations in the principal series is given by $m = 44349{\cdot}0 - 109675/(m + 1{\cdot}0855)^2$, in the first subordinate series by $m = 25236{\cdot}8 - 109675/(m + 0{\cdot}8062)^2$, and in the second subordinate series by $m = 25153{\cdot}0 - 109675/(m + 0{\cdot}6196)^2$. H. M. D.

Spectra of High Frequency. MANNE SIEGBAHN (*Compt. rend.*, 1917, **165**, 59. Compare A., 1916, ii, 362, 405).—A claim for priority over Ledoux-Lebard and Dauvillier (this vol., ii, 283). W. G.

The Spark and the Vacuum Arc Spectra of some Metals in the Extreme Ultra-violet. TOSHIO TAKAMINE and SHIGEHARU NITTA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 117—135).—The wavelengths of lines in the spark spectra of silver, aluminium, gold, bismuth, cadmium, cobalt, iron, manganese, platinum, antimony, and thallium have been measured over the region λ 2000—λ 1830 by using a quartz spectrograph and Schumann plates. In every case, new lines were observed in the most refrangible portion of the ultra-violet region.

The vacuum arc spectra of bismuth, antimony, and thallium were also photographed and several new lines detected for each element in the region λ 2000—λ 1850. H. M. D.

The Occurrence of Harmonics in the Infra-red Absorption Spectra of Diatomic Gases. JAMES B. BRINSMADE and EDWIN C. KEMBLE (*Proc. Nat. Acad. Sci.*, 1917, **3**, 420—425).—With reference to Bjerrum's explanation of the structure of the infra-red absorption bands of gases, an examination has been made of the infra-red spectra of hydrogen chloride and hydrogen bromide. In accordance with the requirements of the quantum hypothesis, first harmonics have been found in the spectra of both gases. The structure of these bands, as well as that of the corresponding weak carbon monoxide band, is found to be in general agreement with theory. Although an attempt was made to detect second and third harmonics in the spectra of hydrogen chloride and carbon monoxide, these experiments gave a negative result. H. M. D.

Qualitative Spectrum Analysis of Organic Dyestuffs by Formánek's Method. JOS. POKORNÝ (*J. Soc. Dyers*, 1917, **33**, 162—166).—A reply to criticisms of the mode of interpreting the spectral observations in Formánek's method of detecting organic dyes. H. M. D.

Inquiries into the Explanation of Radium Disintegration. TARINI CHARAN CHOUDHARI (*Chem. News*, 1917, **116**, 25—27).—The paper discusses the origin of the excess of hydrogen in the radioactive decomposition of water, the loss of weight of a radium salt by disintegration, and the fate of the halogen in radium haloid when the radium disintegrates, directing attention to the unexplained problems in connexion therewith. F. S.

"Spark-lengths" in various Gases and Vapours. ROBERT WRIGHT (T., 1917, **111**, 643—649).—The variation of the length of the spark with the nature of the surrounding gas or vapour has been examined under conditions in which the form of the spark-gap, the temperature, pressure, and the voltage were the same for the different vapours experimented on. The voltage was maintained appreciably constant by arranging an air-gap of definite length in parallel with the vapour-gap, the length of the latter being adjusted so that sparking took place equally through the air- and vapour-gaps when the potential was carefully raised.

For series of chemically comparable substances the length of the vapour-gap decreases with increase in the molecular weight. In other words, the insulating power relative to that of air increases with the molecular weight of the substance. It should, however, be noted that the curves connecting potential and length of spark are not by any means parallel and may intersect one another. This intersection was actually observed in the case of carbon dioxide and air, the former being the better insulator at low potentials, whereas the reverse holds at higher potentials.

H. M. D.

Current Potentials of Electrolyte Solutions. II. H. R. KRUYT (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1021—1028. Compare A., 1914, ii, 837).—In the further investigation of the influence of electrolytes on the current potential, experiments have been made with solutions of hydrochloric acid and *p*-chloroaniline hydrochloride. In both cases the reduction of the current potential is much greater than that produced by potassium chloride. This result can be readily accounted for on the assumption that the phenomenon is dependent on the facility with which the respective cations are adsorbed.

According to Helmholtz's theory, the product of the current potential and the electrical conductivity of the flowing liquid affords a measure of the electric charge on the capillary tube. When the charge of the capillary obtained in this manner is plotted as a function of the concentration of the electrolyte, curves are obtained which show a maximum. In the case of potassium chloride, the maximum corresponds with a much larger concentration than that found for solutions of hydrochloric acid, barium chloride, and *p*-chloroaniline hydrochloride. These observations are obviously closely connected with those which have been made on the influence of electrolytes on the cataphoresis of oil emulsions, and attention is directed to the similarity between the results of these experiments. If the contact charges for the different electrolytes are compared at a concentration greater than those which correspond with the above-mentioned maxima, it is found that the order in which the electrolytes arrange themselves is the same as that which expresses their relative coagulating powers. This again is in favour of the theory that the current potential is largely determined by ion absorption phenomena. H. M. D.

Hydrates of Alcohols and Fatty Acids. II. JOHANNE CHRISTIANSEN (*Zeitsch. physikal. Chem.*, 1917, **92**, 257—274. Compare A., 1916, ii, 75).—A continuation of the work previously published. Experiments are described which indicate that the position of the ballistic electric neutral point of aqueous solutions of alcohols and fatty acids is practically unaffected by change of temperature at low temperatures. It is shown that errors are introduced into the measurements by evaporation during the projection of solution on to the electrode, and as this evaporation is obviously dependent on the condition of the surrounding atmosphere experiments have been carried out in air (*a*) dried with calcium chloride, (*b*) saturated with the solution in question, (*c*) saturated with water vapour, (*d*) saturated with the alcohol or acid vapour, and (*e*) ordinary air. These experiments show that at 0° the errors introduced are unimportant. A series of determinations of the neutral point has therefore been made at 0° for solutions of methyl alcohol, ethyl alcohol, propyl alcohol, trimethylcarbinol, formic acid, acetic acid, propionic acid, and butyric acid in aqueous solutions containing definite quantities of sodium chloride. It is found that the ballistic electrically neutral solutions have compositions corresponding with definite hydrates. The following hydrates are therefore assumed to be present in the solutions: methyl alcohol, $1:2H_2O$; ethyl alcohol, $1:4H_2O$; propyl alcohol, $1:8H_2O$; trimethylcarbinol, $1:16H_2O$; acetic acid, $1:3H_2O$; propionic acid, $1:9H_2O$; and butyric acid, $1:27H_2O$. A theoretical interpretation of the connexion between the ballistic electric neutrality and the presence of a definite hydrate is given in the paper. J. F. S.

Electrolytic Migration. Electrolysis of Solutions of Mixed Alkaline Salts. MARC VAN LAER (*J. Chim. phys.*, 1917, **15**, 154—163).—The electrolysis of solutions of sodium carbonate has been examined from the point of view of current yield. It is shown that the resistance of the cell increases as the electrolysis proceeds owing to the formation and precipitation of sodium hydrogen carbonate. The addition of an oxy-salt of sodium to the carbonate decreases the formation of hydrogen carbonate and makes it possible to obtain directly cathode liquors which are very rich in sodium hydroxide. This addition (of nitrate or sulphate) also brings about a considerable increase in the current yield. The yield may be calculated by the formula of Foerster and Jorre, and since this is based on the transport numbers of the ions it follows directly that the results mentioned above are an immediate consequence of the ionic migration. The mechanism of the migration changes brought about by the addition of an oxy-salt is discussed in the paper. It is shown that by choice of a suitable diaphragm sodium carbonate may be directly and economically converted into sodium hydroxide by the electrolysis of aqueous solutions. J. F. S.

Ultra-microscopic Investigation of very thin Metal and Salt Films obtained by Evaporation in High Vacuum. W. REINDERS and L. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 958—968).—The thin films deposited on the inside of the bulbs of incandescent lamps when various substances are heated to a sufficiently high temperature by the passage of the current through the metallic filament have been subjected to ultra-microscopic examination.

In the case of sodium chloride which has been deposited in these circumstances, the film appears to be optically homogeneous under the ultra-microscope, and it would seem that the sodium chloride is in an amorphous-vitreous condition comparable with that of an undercooled liquid. If the vacuous bulb is opened, so that moist air comes into contact with the film of salt, it quickly becomes opalescent, and the ultra-microscope reveals a network of ultramicrons. In course of time this network becomes distinctly coarser, and ultimately it is possible to recognise the presence of cubic micro-crystals. In dry air, the crystallisation process takes place very slowly, and the vitreous condition may be preserved if the layer of salt is covered by Canada balsam.

Metallic silver, when vaporised and condensed in the above manner yields a film the colour of which changes through greenish-yellow, orange, red, violet, and blue as the thickness increases. Under the ultra-microscope the red, violet, and blue films are distinctly heterogeneous, but the greenish-yellow film is apparently similar in structure to the sodium chloride deposit. Gold closely resembles silver in its behaviour, whilst tungsten only yields films of a grey or black colour, which could not be resolved under the ultra-microscope.

A comparison of the above with metal films obtained by cathode disintegration indicates that the latter consist as a rule of coarser particles than those which are present in the evaporation films.

H. M. D.

Relationship of Heat Capacity to Entropy. VLADIMIR NJEGOVAN (*Zeitsch. physikal. Chem.*, 1917, **92**, 275—286).—A mathematical paper in which it is shown that the heat capacity of a substance is proportional to the absolute value of the entropy. The following equations are developed. These express for gases the dependence of entropy (S) on temperature (T) and pressure (P) on the one hand, and on temperature and volume (v) on the other: $S=2{\cdot}3026C_p^T \log T-4{\cdot}571 \log p_{at}+k$; $S=2{\cdot}3026C_v^T \log T+4{\cdot}571 \log v_1+w$.

J. F. S.

Critical Point, Critical Phenomena, and a few Condensation Constants of Air. J. P. KUENEN and A. L. CLARK (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1088—1098).—A detailed study has been made of the condensation phenomena in the critical region. According to the theory of mixtures, a distinction has to be made between the "plait point" at which the two coexisting phases become identical, and the "critical point of contact," which is the limiting condition for the separation into two phases. The temperature and pressure corresponding with the "plait point" are $-140\cdot73°$ and 37·25 atmospheres, and with the "critical point of contact" $-140\cdot63°$ and 37·17 atmospheres. The density of the liquid at these points is 0·35 and 0·31. The critical density of air calculated from the critical densities of oxygen and nitrogen by the simple mixture rule is 0·34, which lies between the two values given above. H. M. D.

A Simple Exponential Function for the Representation of several Physico-chemical Phenomena. Vapour Tension of Liquids and Solids, Dissociation Pressure, Equilibrium Constants, Densities of Liquids and Vapours, and Radiation from Black Bodies. ALBERT SCHMIDT (*J. Chim. phys.*, 1917, **15**, 97—153).—A theoretical paper in which it is shown that the expression $\log p/p_1 = f_1 - k/\delta$ is more suited to the calculation of the vapour pressure of liquids and solids at different temperatures than the empirical formula of van der Waals. This expression contains two constants, k and δ, of which δ represents the temperature of origin, a temperature characteristic of the substance and different from the absolute zero, and k is a function of this temperature. A method is described by which these two constants may be graphically evaluated from known experimental data. Tables of the values of these constants are given for 114 liquid substances and 27 solid substances. The calculation of the vapour pressure of 14 substances, boiling between $-186°$ (argon) and $+925°$ (zinc), at various temperatures shows extremely well that the formula represents the change of pressure as a function of the temperature. The calculated values agree sufficiently well with the experimental values of different observers. This same formula has in twelve cases been applied to the calculation of the dissociation pressure at different temperatures. Tables of the calculated values are given along with the experimentally determined values; the agreement is particularly good. Some examples are given which show that this same relationship is equally applicable to the variations of the equilibrium constant of a gaseous system. Among other things, it is also shown that this formula represents the changes of the product of the liquid and gaseous densities of substances with change of temperature. The values of the constants have been calculated for 37 substances, and the value of the product has been calculated for chlorine and ether over a wide range of temperature. In both cases the results are in excellent agreement with the observed values of Young and Pellaton except at the higher temperatures, where considerable divergence is manifested. In these cases the calculation of the liquid density and the density of the saturated vapour shows that the combination of the present formula with the law of rectilinear diameters is capable of reproducing the changes of density of the two phases with temperature up to about 40° of the critical temperature. Finally, it is shown that this same formula is applicable to the radiation of absolutely black bodies at different temperatures. Tables are given showing the agreement between (*a*) the luminous radiation and (*b*) the total radiation, with the observed values for temperatures between 100·1° and 1780°.

J. F. S.

Methods and Apparatus used in the Cryogenic Laboratory. XVII. Cryostat for Temperatures between 27° and 55° (absolute). H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1049—1058).—An apparatus is described which makes it possible to maintain constant temperatures over the range 27—55° absolute. This is attained by passing cooled gaseous hydrogen through liquid hydrogen contained in a specially constructed evaporator, the gas thus obtained, after being heated to the desired temperature, being conducted into the cryostat in which the experimental chamber is immersed. Experience has shown that the hydrogen vapour cryostat permits of the maintenance of temperatures for considerable intervals of time within the specified range with deviations which do not exceed 0·01°.

H. M. D.

Isothermals of Monatomic Substances and their Binary Mixtures. XVIII. A Preliminary Determination of the Critical Point of Neon. H. KAMERLINGH ONNES, C. A. CROMMELIN, and P. G. CATH (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1058—1062).—The construction of the thermostat described in the preceding abstract has enabled the authors to determine with accuracy the critical data for neon. The values found are: critical temperature, −228·35°; critical pressure, 26·86 atmos.

H. M. D.

A Method of Determining Molecular Weights. ÉDOUARD URBAIN (*Compt. rend.*, 1917, **165**, 65—67).—A mixture of two non-miscible, volatile liquids is distilled, and the distillate analysed. Using one liquid the constants of which are known, the vapour density of the second liquid is given by $d_1 = dpq_1/(H-p)q$, where d, p, and q are respectively the vapour density, pressure, and weight of the known liquid in 100 grams of distillate, d_1 and q_1 the corresponding constants for the liquid the molecular weight of which is being determined, and H the pressure under which the mixture is distilled. From the vapour density, the molecular weight of the liquid under examination can readily be calculated.

W. G.

The Additivity of the Specific Volume in Sols. H. R. KRUYT (*Kolloid Zeitsch.*, 1917, **20**, 239—242).—From measurements of the density of colloidal solutions, Wintgen (A., 1915, ii, 751) drew the conclusion that the volume relations in colloidal systems are exactly similar to those exhibited by true solutions. This conclusion is criticised, although it may be admitted that deviations from the mixture rule will be comparatively small in the case of colloidal solutions.

H. M. D.

Measurement of Surface Tension by the Method of the Weight of Drops. F. Louis Perrot (*J. Chim. phys.*, 1917, **15**, 164—207, and *Arch. Sci. phys. nat.*, 1917, [iv], **43**, 476—486).—A review and criticism of the recent work on this subject, in which it is shown that the classic formula of the proportionality of the weight of a drop to its surface tension, $P=2\pi r\gamma$, ought to be definitely abandoned, since it is only a false approximation. The theory of Lohnstein, despite its static and capillary basis, may with advantage be tentatively allowed to replace the older formula. For physico-chemical investigations the method of Morgan, when subjected to the conditions and limitations placed on it by him, may be regarded as satisfactory. Up to the present no relationship between the weight of a falling drop and its other properties has been found. A bibliography of the literature of the subject from 1899 is appended to the paper. J. F. S.

Surface Tension and Cohesion in Metals and Alloys. Sydney W. Smith (*J. Inst. Metals*, 1917, **17**, 65—118. Compare A., 1915, ii, 44).—The relations between surface tension and other physical properties of metals and alloys are discussed. Cases of liquation, as in the freezing of alloys of silver and copper, are explained by the considerable differences between the surface tensions and intrinsic pressures of the component metals. When the surface tensions and intrinsic pressures are practically equal, as in the alloys of gold and silver, or of silver and cadmium, liquation does not take place. The maximum hardness in a series of solid solutions usually occurs at a composition at which the products of the atomic percentages and the respective intrinsic pressures are equal. C. H. D.

The Viscosity of Liquefied Gases. VI. Observations on the Torsional Oscillatory Movement of a Sphere in a Viscous Liquid with Finite Angles of Deviation and Application of the Results obtained to the Determination of Viscosities. VII. The Torsional Oscillatory Motion of a Body of Revolution in a Viscous Liquid. VIII. The Similarity in the Oscillatory Rotation of a Body of Revolution in a Viscous Liquid. J. E. Verschaffelt (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1062—1073, 1073—1079, 1079—1084).—A series of theoretical papers dealing with the oscillatory motion of a sphere or similar bodies of revolution in viscous media and the application of the method to the determination of the viscosities of fluids. H. M. D.

The Viscosity of Liquefied Gases. IX. Preliminary Determination of the Viscosity of Liquid Hydrogen. J. E. Verschaffelt and Ch. Nicaise (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1084—1088).—In consequence of the low value of the viscosity of liquid hydrogen, the damping of the oscillatory motion is very slight and the internal friction of the suspension wire is a factor of considerable importance in the determination. Experiments showed that the internal friction at this low temperature varied within wide limits and was difficult to control. On this account the accuracy attainable is limited and the approximate value of the viscosity of liquid hydrogen at 20·36° abs. is given as 0·00011. The density of the liquid is 0·0708. H. M. D.

Fluidity. I. C. Drucker (*Zeitsch. physikal. Chem.*, 1917, **92**, 287—319).—A theoretical paper in which the following points are discussed at length: (*a*) viscosities of gases and gaseous mixtures; (*b*) viscosity and vapour pressure; (*c*) fluidity of liquid mixtures; and (*d*) fluidity and heat of fusion. Numerous curves and tables of results of other workers are introduced into the paper to illustrate the points raised in the discussion. It is shown that the viscosity of gases and liquids is closely related to surface phenomena; the effect of movement on the individual layers, and in particular on the layer adsorbed by the solid contact layer, can be referred to the dual influence of the viscosity-coefficient and the adsorptive-coefficient. The fluidity of liquid substances at different temperatures bears an almost linear relationship to the vapour pressure. The fluidity of binary liquid mixtures corresponds with a linear mixture formula, even when a chemical combination between the two liquids is present. In the latter case instead of a binary formula, a ternary or even a formula of a higher degree is necessary to represent the relationship. If, however, the complex or combined condition is sensitive to the volume change induced by movement, then a mixture formula can in no way represent the case. It is possible to calculate the heat change from the temperature-coefficient of the fluidity; this heat change is very close in value to the heat of fusion, and often is identical with it. The heat change of the spacial orientation of the crystals constitutes generally only a very small fraction of the heat of solidification.

J. F. S.

An Improved Bunsen Diffusion Apparatus. Jerome S. Marcus (*J. Ind. Eng. Chem.*, 1917, **9**, 603).—A description of a modified all-glass apparatus designed to facilitate the introduction of the gas under investigation.

The gas is introduced by a three-way tap which later connects the diffusion tube with the aperture, the entry of the gas being regulated by running mercury from another three-way tap situated in the lowest part of the bend of the U-tube between the diffusion tube and the mercury reservoir. The reservoir is of considerable cross-section, and is filled to the same level for each experiment so as to give a constant initial head of mercury. D. F. T.

Studies of Solution. I. The Change of Molecular Solution Volumes in Solutions. Shinkichi Horiba (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 1—43).—The method of Forch (A., 1903, ii, 714) has been used to calculate the molecular volumes of solute and solvent in aqueous solutions of sucrose, potassium chloride, sodium chloride, and ammonium chloride at temperatures ranging from 0° to 50°. The curves obtained by plotting the molecular solution volume against the concentration show that the water contracts, the molecular volume of the solvent decreasing with increase in the concentration. Similarly, the curves for the solute show that this expands, the volume increasing with the concentration, although the rate of increase diminishes as the concentration increases.

The contraction of the solvent, which is brought about by admixture with the various solutes, is discussed with reference to the osmotic pressure of the solution and Tammann's internal pressure, and a modified method of calculating the internal pressure is described.

By reference to the molecular volumes of a large number of organic substances which are only sparingly soluble in water, it is shown that, in general, the solubility decreases with increase in the magnitude of the molecular volume. H. M. D.

Studies of Solution. II. A Conception of Osmotic Pressure. SHINKICHI HORIBA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 45—57).—A theoretical discussion of the nature and origin of osmotic pressure, in which it is suggested that the contraction of the solvent in solution (see preceding abstract) may be responsible for the effects which are generally attributed to the existence of so-called osmotic pressure. H. M. D.

Rhythmic Diffusion Structures in Gelatin-Salt Jellies. I. W. MOELLER (*Kolloid Zeitsch.*, 1917, **20**, 242—250).—In a previous paper (this vol., ii, 132) the author has put forward the view that gelatin jellies contain two substances, one of which, α-gelatin, forms a structural network, the spaces in which are occupied by β-gelatin, which is structureless. It is now suggested that rhythmic changes in the structure of the fibrillar network are responsible for the separation of foreign substances in rhythmically distributed layers. According to this view, the development of the structures known as Liesegang's rings is not dependent on the chemical interaction of substances after diffusion through a jelly medium, and such alternating layers may make their appearance when the substance deposited is that contained in the jelly, and not the product of the reaction of this substance with a second.

Experiments made with gelatin jellies containing sodium chloride show that rhythmic structures are developed when such jellies are brought into contact with solutions of hydrochloric acid. Chemical interaction in the ordinary sense does not take place in this system. It is assumed that the rate of diffusion of the acid is greater in the case of fibrillar systems which are characterised by a radial disposition of the fibril elements than in those systems the structural elements of which are oriented in a direction at right angles to the radial. Forces are thus called into play which indirectly determine a rhythmic alternation in the coagulation of the sodium chloride.

The structures which have been observed under prescribed conditions are illustrated by a series of photographs. H. M. D.

In-, Uni-, and Bi-variant Equilibria. XV. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 999—1006. Compare this vol., ii, 299).—The equilibrium relations in heterogeneous systems are further discussed, and a summary is given of the various possible types of pressure–temperature diagrams. H. M. D.

The Temperature-coefficient of a Heterogeneous Reaction. R. G. VAN NAME (*Amer. J. Sci.*, 1917, [iv], **43**, 449—460).—The influence of temperature on the rate of dissolution of metallic cadmium in an aqueous solution of iodine has been determined by measurements at 0°, 15°, 25°, 35°, 45°, 55°, and 65°. The method used has been described in an earlier paper (A., 1911, ii, 973). The value of the temperature-coefficient for 10° rise in temperature varies from 1·35 for the lowest to 1·19 for the highest temperature interval, and is consequently of the same order of magnitude as the temperature-coefficient for the diffusion of a binary electrolyte. In agreement with this it is found that the curves obtained by plotting the rate of dissolution and the fluidity of the solution against the temperature are of the same type. The rate of increase of the fluidity with temperature is, however, somewhat smaller.

Over the temperature range examined, the velocity of dissolution of the metal is proportional to the product of the fluidity of the solution and the absolute temperature. This relationship is in accord with Einstein's diffusion formula, and the facts generally are regarded as affording evidence in support of the diffusion theory of heterogeneous reaction. H. M. D.

A Contribution to the Energy Theory of Matter. H. STANLEY REDGROVE (*Chem. News*, 1917, **116**, 37—40).—Evidence is put forward in support of the view that additive properties of substances may be evaluated in terms of the number and type of the valency bonds. The substances dealt with by the author are all organic compounds, and for these it is shown that the molecular weight, the molecular heat of combustion, the molecular refractivity, and the molecular volume can be regarded as functions of the number and type of the valency bonds in the molecules.

By a mathematical argument, it is further shown that any property which can be attributed to, or treated as a function of, the number and nature of the constituent atoms can *ipso facto* be attributed to, or treated as a function of, the number and type of the valency bonds. H. M. D.

Inorganic Chemistry.

Volumetric Relationship of the Combination of Hydrogen and Oxygen, $2H_2:O_2$, and the Atomic Weight of Hydrogen. PH. A. GUYE (*J. Chim. Phys.*, 1917, **15**, 208—214).—A theoretical paper in which the volume ratio of the combination of hydrogen and oxygen as found by different methods is critically discussed. On the one hand, the ratios of Scott (A., 1893, ii, 515), 2·00285, and of Burt and Edgar (A., 1916, ii, 427), 2·00288, are compared with the physico-chemically calculated values of Rayleigh, 2·00304, of Jaquerod and Scheuer, 2·00298, of Chappius and of Gray and Burt, 2·00308. The effect of these two sets of values on the atomic weight of hydrogen is considered, and it is concluded that for this value the rounded figure 1·0077 should be adopted. J. F. S.

Preparation of Alkali Percarbonates. ROESSLER AND HASSLACHER CHEMICAL CO. (U.S. Pat., 1225832; from *J. Soc. Chem. Ind.*, 1917, **36**, 712).—Hydrogen peroxide and an alkali carbonate are allowed to react in the presence of a restricted quantity of water, common salt being added to aid the separation of the percarbonate. A silicate of magnesium is employed as a stabilising agent. D. F. T.

Double Salt Formation between Nitrates and Sulphates in Aqueous Solution. A. MASSINK (*Zeitsch. physikal. Chem.*, 1917, **92**, 351—380).—The author has investigated the following systems at the temperatures indicated: (1) $(NH_4)_2SO_4$–NH_4NO_3–H_2O (0°, 30, 70°); (2) K_2SO_4–KNO_3–H_2O (35°); (3) Li_2SO_4–$LiNO_3$–H_2O (25°, 35°); (4) $CuSO_4$–Na_2SO_4–H_2O (20°, 35°); (5) $CuSO_4$–$Cu(NO_3)_2$–H_2O (20°); (6) $Cu(NO_3)_2$–$NaNO_3$–H_2O (20°); (7) Na_2SO_4–$NaNO_3$–H_2O (10°, 20°, 25°, 30°, 34°, 35°); and (8) $CuSO_4$–$Cu(NO_3)_2$–$NaNO_3$–Na_2SO_4–H_2O (20°). The isotherms for long series of mixtures in each case were determined, both solid and liquid phases being analysed in each case. It is shown that the double salts $9Li_2SO_4,LiNO_3,27H_2O$ and $11Li_2SO_4,LiNO_3,17H_2O$ exist at 35°, but not at 25°. The saturation curve of Li_2SO_4,H_2O is composed of two distinct branches. The compound

$$NaNO_3,Na_2SO_4,H_2O$$

exists at a minimum temperature 12·8° where it occurs as the stable solid phase; at 32° it disappears as stable solid phase, although at 35° it still appears as metastable solid phase. The compound $3NaNO_3,4Na_2SO_4$ is stable between 20° and 35°. The compound $3NaNO_3,2Na_2SO_4$ is stable between 30° and 35°. The lowest temperature at which anhydrous sodium sulphate is stable in the system $NaNO_3$–Na_2SO_4–H_2O is found to be 24·2°. In the quaternary system $NaNO_3$–Na_2SO_4–$CuSO_4$–$Cu(NO_3)_2$–H_2O no new double salts were found at 20°, the only compound appearing as solid phase at this temperature being $NaNO_3,Na_2SO_4,H_2O$.

J. F. S.

The Phosphates of Calcium. IV. The Basic Phosphates. HENRY BASSETT, jun. (T., 1917, **111**, 620—642. Compare A., 1908, ii, 675).—The conditions of equilibrium in the system $CaO-P_2O_5-H_2O$ have been further investigated by experiments covering the region lying between those which are characterised by the existence of dicalcium hydrogen phosphate and calcium hydroxide as stable solid phases. Observations were made at 25°, 100°, and 170—200°. At the lowest temperature, the equilibrium condition is attained only after very long intervals of time.

It is shown that tricalcium phosphate and hydroxyapatite, $3Ca_3(PO_4)_2,Ca(OH)_2$, are the only two phosphates which can exist in stable equilibrium with an aqueous solution at 25°. This is probably the case at all temperatures.

The ratio of $CaO:P_2O_5$ in the solutions with which hydroxyapatite can exist in stable equilibrium extends over a considerable range, from solutions, on the one hand, which are faintly acid to a point which is quite close to that corresponding with a solution of pure calcium hydroxide. There is no evidence of the existence of phosphates between dicalcium hydrogen and tricalcium phosphate, nor of the formation of solid solutions as stated by Cameron, Seidell, and Bell (A., 1906, ii, 163, 164). It is considered probable that hydroxyapatite is the only calcium phosphate which can exist in stable form under normal soil conditions.

The nature of bone phosphate is discussed, and it is suggested that this represents a mixture of hydroxyapatite and calcium carbonate with small quantities of adsorbed hydrogen carbonates of sodium, potassium, and magnesium. H. M. D.

The Solubility of Calcium Phosphates in Citric Acid. A. A. RAMSAY (*J. Agric. Sci.*, 1917, **8**, 277—298).—The author finds that the substances commonly sold as "phosphate of lime" and "Calcii Phosphas B.P." are mixtures of di- and tri-calcium phosphates. The methods generally used for the preparation of calcium phosphate yield a mixture of di- and tri-calcium phosphates and calcium hydroxide. Pure tricalcium phosphate is obtained by acting on calcium oxide with phosphoric acid in the proportion of $3CaO:1P_2O_5$, and separating the precipitate within an hour. So prepared, about 91% of the total phosphoric acid is soluble in 2% citric acid, using the standard method for this determination. This solubility is reduced to 84·5% if 25% of calcium carbonate is first added to the calcium phosphate. Further addition of another 25% of calcium carbonate only reduces the solubility of the phosphoric acid to 84·3%. In this determination, the whole of the excess of calcium is dissolved during the thirty minutes' extraction with the 2% citric acid. Since both tricalcium and dicalcium phosphates are soluble in the 2% citric acid solution, the method of differentiating between these two forms of phosphate by the selective action of this solvent is unsatisfactory (compare preceding abstract). W. G.

An Apparatus for the Purification of Mercury. HARRISON E. PATTEN and GERALD H. MAINS (*J. Ind. Eng. Chem.*, 1917, **9**, 600—603).—A detailed description of an apparatus embodying various suggested processes for the purification of mercury. The metal is broken into fine threads by passage through bolting silk, the threads during their subsequent fall through dilute nitric acid being made the anode of an electrolytic process. The mercury is automatically returned to the top, being raised by a current of air working on the injector principle; during this return journey, some oxidation of impurities occurs, and this effect is increased by having the return tube surrounded with a heating coil. After circulating 300 times, the purified mercury is twice distilled, first in a current of air and then in a vacuum. Most of the mercury lost by dissolving into the acid can be recovered by precipitation as calomel. D. F. T.

A Simple Method for the Purification of Mercury. Horace Barratt Dunnicliffe (*Chem. News*, 1917, **116**, 41—42).—The apparatus consists of a retort supported in such a manner that the neck is vertical, with the open end protruding into a covered beaker in which the purified mercury is collected. Through the tubulure of the retort passes the stem of a dropping funnel and also a piece of narrow glass tubing.

The mercury to be purified is subjected to a preliminary purification by the usual methods, and is then subjected to distillation in the apparatus. The tap of the dropping funnel is adjusted so that mercury drips into the retort at about the same rate as it is removed by distillation. This occurs at the rate of 400—500 grams per hour. All parts of the apparatus are cleaned by treatment with sodium hydroxide, acids, and dichromate mixture, and then washed with distilled water and dried by a current of dust-free hot air. H. M. D.

Aluminium Production by Electrolysis. The Mechanism of the Reaction. Richard Seligman (*J. Inst. Metals*, 1917, **17**, 141—144).—It has generally been assumed that aluminium is formed by the reaction $Al_2O_3+3C=3CO+2Al$ when a carbon anode is used. Actually the consumption of carbon may be much lower, and analyses of the anode gases, collected by enclosing one of the anodes in a sheet metal bell, show as much as 45·6% of carbon dioxide when the temperature is 945°, the proportion diminishing with rise of temperature. In laboratory experiments, heating externally to avoid excessively high current densities, gases containing more than three volumes of carbon dioxide to one of monoxide have been obtained. It is uncertain whether the reaction should be represented by $2Al_2O_3+3C=4Al+3CO_2$, or whether the primary anodic product is oxygen, which reacts with the carbon anode in a manner dependent on temperature, current density, rate of removal of gas, and other factors. C. H. D.

Mechanism of the Tempering of Carbon Steels. P. Chevenard (*Compt. rend.*, 1917, **165**, 59—62. Compare this vol., ii, 372).—A study of the cooling of carbon steels in hydrogen, nitrogen, or mixtures of these two gases, the velocities of cooling being varied. The results obtained confirm the conclusions of Portevin and Garvin (compare this vol., ii, 372). Tempering results from a displaced transformation at low temperatures. This transformation is incomplete, and the martensite encloses a certain proportion of the metal in a state stable at higher temperatures. For a given method of cooling, the maximum temperature of annealing, θ_0, and the minimum temperature of tempering, θ_1, are higher and more widely separated the slower is the velocity of cooling. W. G.

Manganese Steels. A. PORTEVIN (*Compt. rend.*, 1917, **165**, 62—65).—By annealing, followed by very slow cooling of steels containing 7% manganese and 0·5—1·0% carbon, it is possible to obtain lamellar perlite with martensite. With a steel containing 12% manganese and 1% carbon, by very slow cooling the co-existence of lamellar perlite and austenite separated by a thin border of troostite can be obtained. By ordinary annealing the whole becomes austenitic. Using a steel containing 9·8% manganese and 0·66% carbon, by slow cooling it was possible to find the complexes troostite–perlite–martensite–austenite, the martensite arising from a polymorphic transformation of the austenite. W. G.

Monoclinic Double Selenates of the Nickel Group. A. E. H. TUTTON (*Phil. Trans.*, 1917, *A*, **217**, 199—235).—This communication deals with the morphology and optical properties of crystals of the four double selenates of the series

$$R_2M(SeO_4)_2,6H_2O,$$

in which M is nickel and R is potassium, rubidium, cæsium, or ammonium. They belong to the large monoclinic isomorphous series of double sulphates and selenates, of which ferrous ammonium sulphate is the most familiar example. Great care has been taken in every case to obtain the most perfect crystals for examination, and their morphological and optical properties have been fully investigated. They belong to the holohedral prismatic class of the monoclinic system, the symmetry plane is the optic axial plane, and, except in the case of the cæsium salt, the double refraction is positive. The dimensions of the optical ellipsoid have been determined in each case.

Potassium nickel selenate: $a:b:c=0·7467:1:0·5059$; $\beta=104°27'$; D_4^{20} 2·559; M.V.=206·14.

Rubidium nickel selenate: $a:b:c=0·7395:1:0·5031$; $\beta=105°20'$; D_4^{20} 2·856; M.V.=216·96.

Caesium nickel selenate: $a:b:c=0·7288:1:0·4993$; $\beta=106°11'$; D_4^{20} 3·114; M.V.=229·17.

Ammonium nickel selenate: $a:b:c=0·7395:1:0·5048$; $\beta=106°17'$; D_4^{20} 2·243; M.V.=216·53.

A careful comparison of the four salts with respect to all the properties subjected to accurate measurement has been made, with the result that the author's previous conclusions regarding the morphotropic relationship between ammonium and the alkali metals is fully confirmed. The axial ratios and molecular volumes of the rubidium and ammonium salts are almost identical; hence their structural units, the dimensions of which are given by the topic axial ratios, are congruent. For the bearing of these results on the law of valency volumes, see this vol., ii, 244. E. H. R.

Recovery of Molybdenum Residues. VICTOR LENHER and M. P. SCHULTZ (*J. Ind. Eng. Chem.*, 1917, **9**, 684—685).—A description of a method based on the separation of the molybdenum as sulphide.

Waste molybdate liquors are diluted or treated with alkali so that the amount of free nitric acid is reduced to 0·1—0·4%. Hydrogen sulphide is then passed into the solution, preferably warm, and the precipitated molybdenum sulphide is washed and dried, after which it may be converted into the trioxide by roasting.

Ammonium phosphomolybdate is dissolved in sufficient aqueous sodium hydroxide to give a solution just alkaline to phenolphthalein; the liquid, after filtration if necessary, is treated with hydrogen sulphide, and the molybdenum sulphide precipitated by acidifying with dilute hydrochloric acid. D. F. T.

Zirconyl Acid Sulphate. ED. CHAUVENET (*Compt. rend.*, 1917, **165**, 25—28).—A study of the neutralisation of the acid sulphate, $SO_4\colon ZrO,SO_3$, in *N*/1000-solution with *N*/1000-sodium hydroxide gives two sharp changes, the first corresponding with the formation of the normal sulphate and the second with the formation of a basic sulphate, $SO_4\colon ZrO,ZrO_2$. Thus the most stable state of the system ZrO_2 and SO_3 is the latter form. The compounds of the zirconyl radicle have a great tendency to yield compounds of the type $A\colon ZrO,ZrO_2$. W. G.

The Occurrence of Germanium in Missouri and Wisconsin Blendes. G. H. BUCHANAN (*J. Ind. Eng. Chem.*, 1917, **9**, 661—663. Compare A., 1916, ii, 486).—Small quantities of germanium are present both in Wisconsin and Missouri zinc ores and tend to become concentrated in the residues remaining in the retorts, so that oxide of zinc prepared from spelter residues may contain a considerable proportion of germanium.

The method adopted for testing zinc oxide for traces of germanium consisted of mixing 100 grams with 200 c.c. of concentrated hydrochloric acid and distilling to about one-half the volume in a current of chlorine, collecting the distillate by means of a water-cooled condenser. The distillate was diluted with an equal bulk of water and treated with hydrogen sulphide for half an hour; if no other precipitate than sulphur is obtained, germanium is absent. The nature of the precipitate was confirmed by dissolving in boiling water, re-precipitating with hydrogen sulphide in the presence of hydrochloric acid, dissolving the new precipitate in aqueous ammonia, evaporating to dryness, and igniting the residue; the solution of the residue in a little water, on addition of hydrofluoric acid and saturation with potassium chloride, should, if germanium is present, give a bulky, grey precipitate, soluble on heating or on the addition of water. D. F. T.

Mineralogical Chemistry.

Eakleite, a New Mineral from California. ESPER S. LARSEN (*Amer. J. Sci.*, 1917, [iv], **43**, 464—465).—A small specimen labelled "Wollastonite, St. Inez, Calif." in the museum of the University of California was found on optical examination to represent a new species, for which the name *eakleite* is proposed. It is pale pink with a fibrous structure, and resembles pectolite in appearance. D 2·685—2·705; H 6½; fusibility, 2½; readily decomposed by acids with separation of flaky silica. It is optically positive, with a very small axial angle; the direction of extinction (γ) is parallel to the fibres; refractive indices (Na) $\alpha = \beta = 1{\cdot}583$, $\gamma = 1{\cdot}593$. The following mean of two analyses by A. S. EAKLE corresponds with the formula $5CaO,5SiO_2,H_2O$, representing perhaps a calcium pectolite:

SiO_2.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
50·17	1·04	45·45	trace	nil	nil	3·18	98·84

L. J. S.

The Constitution of Melilite and Gehlenite. FRANK WIGGLESWORTH CLARKE (*Amer. J. Sci.*, 1917, [iv], **43**, 476—484).—The recent paper by Schaller on these minerals (A., 1916, ii, 632) is discussed, and the analyses recalculated as mixtures of the following molecules: $Al_4(SiO_4)_6Ca_4Na_4$ (soda-lime-sarcolite), $Al_4(SiO_4)_6Ca_6$ (sarcolite), $Al_2(SiO_4)_6Ca_9$ ('normal melilite'), $Al_4(Si_3O_8)_6Ca_4Na_4$, and $Al_2(SiO_4)_6Ca_6(AlO_2Ca)_6$. The last two of these are hypothetical, the former, a trisilicate, to express the excess of silica over the orthosilicate ratio met with in melilite, and the latter, with the basic univalent group, AlO_2Ca, to explain the deficiency of silica in gehlenite.

These molecules are represented graphically in accordance with the author's theory of the silicates (A., 1897, ii, 50), and the genetic and paragenetic relations of these and other allied minerals (anorthite, garnet, epidote, idocrase, scapolite) are discussed. As substitution derivatives of the normal aluminium orthosilicate, $Al_4(SiO_4)_3$, the following alumosilicic acids are now postulated: $Al_3(SiO_4)_3H_3$ ('trialic' acid, for example, anorthite is calcium 'trialate'); $Al_2(SiO_4)_3H_6$ ('dialic' acid, for example, garnet and sarcolite are calcium 'dialates'); and $Al(SiO_4)_3H_9$ ('unalic' acid, for example, the melilite silicate is calcium 'unalate'). L. J. S.

Analytical Chemistry.

An Automatic Suction Attachment for an Ordinary Pipette. J. P. Schroeder (*J. Ind. Eng. Chem.*, 1917, **9**, 687—688).—To the ordinary mouthpiece of the pipette is attached by means of rubber tubing a three-way tap, one of the remaining tubes of which is open to the atmosphere, whilst the other serves for the application of the necessary suction by means of a pump. In order to facilitate the exact filling of the pipette, a groove is filed on the surface of the barrel of the tap across the edges of the bored hole so that the suction may be cut off gradually.

If the pipette is cut short at its graduation mark, the shortened stem being passed through a bung and fitted by this into a wider glass tube, which is then attached to the three-way tap, the pipette cannot be filled beyond the mark, and the necessity for the careful regulation of the suction is reduced. D. F. T.

A Modified Soxhlet Extractor. D. F. Twiss and W. McCowan (*J. Soc. Chem. Ind.*, 1917, **36**, 692).—A description of a glass continuous extraction apparatus, somewhat resembling that of Blount (*Analyst*, 1888, **13**, 127), but with the outer jacket reaching only to a level just above the aperture by which the vapour of the solvent passes into the extraction cup. The apparatus is thereby rendered stronger and the condensation of vapour in the outer jacket is decreased. By restricting the size of the aperture by which the vapour passes from the outer jacket into the inner cup, an excess of temperature in the outer jacket can be maintained sufficient to keep the liquid in the inner cup in steady, quiet ebullition. D. F. T.

A New, Practical Colorimeter. E. Moreau (*Ann. Falsif.*, 1917, **10**, 235—237).—The apparatus consists of a flat-bottomed, graduated tube of the same internal diameter as the ordinary comparison tubes, which has sealed in near the lower end a lateral tube connected by rubber tubing to a reservoir, containing the standard comparison solution. A known volume of the solution under examination is placed in the comparison tube together with the necessary reagent, and the tube is placed alongside the graduated tube, into which is then allowed to flow the standard solution and reagent, until the depth of colour in the two tubes viewed vertically is identical. The amounts of the constituent to be determined present in the two tubes are inversely proportional to the volumes of liquid used. W. G.

Method of Rendering More Sensitive Colorimetric Analyses. Georges Le Roy (*Ann. Falsif.*, 1917, **10**, 208—210).—In the colorimetric analysis of water, for the purposes of estimating the amount of an unstable constituent, such as free chlorine, present in quantity so small as not to be detected by the ordinary methods, a known, sufficient amount of chlorine is added to the water to bring it within the limits of detection, and then the ordinary colorimetric estimation is performed. W. G.

Potassium Hydrogen Carbonate as an Analytical Standard. G. Bruhns (*Chem. Zeit.*, 1917, **41**, 386—388).—The author confirms the conclusion previously arrived at by Winkler (A., 1915, ii, 647) and Incze (A., 1916, ii, 146) that potassium hydrogen carbonate is a trustworthy analytical standard for all but extremely accurate work. It may be prepared even more simply than these authors suggest by allowing the ordinary "pure" salt in fine powder to remain exposed for several hours in a dry room. Standardised against fused sodium chloride, a sample prepared in this way was found to be correct to 0·02%. Solutions stronger than $N/10$ should not be employed, owing to the tendency to evolve carbon dioxide, which is exhibited by concentrated solutions. G. F. M.

Theory of the Electrolytic Estimation of the Halogens as Silver Haloids. A. H. W. Aten (*Zeitsch. physikal. Chem.*, 1917, **92**, 320—344).—A theoretical paper in which the theory of the electrolytic estimation of halogens as silver haloids is developed on the basis of the Nernst diffusion theory. The course of the diffusion curves of silver ions and halogen ions is calculated, as well as the quantity of silver haloid which is deposited in the solution and its distribution over the diffusion layer. The form of the theoretical current potential curve for a silver anode in a solution of a haloid is determined, and the fractions of the current which are used in the formation of the silver haloid on the anode and in the solution are evaluated. From the ratio of these two fractions the smallest possible error of the analysis is calculated. It is thus shown that under suitable conditions the estimation of chloride is very accurate, and that of the other haloids much more so. The current potential curves for chlorides, bromides, and iodides with a silver anode have been experimentally determined and compared with the theoretically developed curves. A sufficient agreement between the two sets of curves is demonstrated. J. F. S.

Estimation of Free Chlorine in Hypochlorite Solutions. F. Dienert and F. Wandenbulke (*Compt. rend.*, 1917, **165**, 28—29).—Working with dilute solutions containing not more than 0·5 gram of free chlorine per litre, the following method gives a ready means of estimating the free chlorine. Five c.c. of the hypochlorite solution are diluted to the above degree with water, and ammonium sulphate to the extent of at least 150 parts for every part of free chlorine is added and a few crystals of potassium iodide. The iodine set free is then titrated with standard arsenious acid solution. W. G.

Microreactions of the Perchloric Ion. G. Denigès (*Ann. Chim. anal.*, 1917, **22**, 127—128).—Use is made of the characteristic properties of the perchlorates of certain alkaloids (compare this vol., ii, 345) for the detection of the perchloric ion. Either a 1% solution of strychnine sulphate in water or a 2% solution of brucine in dilute acetic acid, or a 2% solution of morphine hydrochloride is used, one drop being added to a drop of the solution under examination on a microscope slide. The resulting crystals are examined under the microscope. With strychnine, 1 part of perchloric ion in 1000; with brucine, 2—3 parts in 1000, and with morphine, 5 parts in 1000 can be detected. W. G.

Argentometric Estimation of Bromides and Iodides. I. M. Kolthoff (*Pharm. Weekblad*, 1917, **54**, 761—766).—Iodides can be estimated in the presence of 20% of chlorides and 2% of bromides by silver nitrate in sulphuric acid solution, with starch iodide as indicator. A. J. W.

Volumetric Estimation of Sulphur in Pyrites. T. J. I. Craig (*Chem. News*, 1917, **115**, 253—255, 265—268).—A method is described for the volumetric estimation of sulphur in pyrites based on its oxidation to sulphuric acid by means of aqua regia, or preferably nitric acid and bromine, and titration with standard alkali hydroxide after the removal of all the other acid ions from the solution. It is shown that nitric acid is completely eliminated from the aqua regia solution of pyrites by evaporating to dryness twice with hydrochloric acid, and finally drying for an hour at 110°, whilst from the nitric acid–bromine solution two evaporations to dryness, followed by an hour's heating at 110°, is sufficient to remove both nitric acid and bromine. Where hydrochloric acid is present, it can only be completely eliminated by treating the solution with silver oxide, the alternative being to estimate it with standard silver nitrate and make the requisite allowance in the subsequent titration of the sulphuric acid. When arsenic acid is present it is shown to be practically all eliminated by the precipitated ferric hydroxide, and hence does not interfere with the titration. The procedure recommended is briefly as follows: 10 grams of pyrites are treated with 30% nitric acid, the reaction mixture cooled to 50°, treated with 5 c.c. of bromine, and boiled until no more brown fumes are liberated. Nitric acid is eliminated as above described, and the residue dissolved in water and made up to 250 c.c. Of this solution 25 c.c. are boiled with a known excess of *N*-sodium hydroxide and the solution made up to 200·25 c.c. (0·25 c.c. to allow for the volume occupied by the ferric hydroxide). After filtration, an aliquot portion is titrated to neutrality with phenolphthalein as indicator. The results obtained are claimed to be closely in accord with those obtained by the more elaborate gravimetric method. The paper includes a short historical summary of the various methods suggested for the estimation of sulphur in pyrites. G. F. M.

The Estimation of Free Sulphur Trioxide in Fuming Sulphuric Acid by Titration with Water. R. G. Parker (*J. Soc. Chem. Ind.*, 1917, **36**, 692—694).—The author finds that the amount of sulphur trioxide in fuming sulphuric acid can be accurately estimated by titrating a weighed quantity of the acid in a stoppered cylinder with water until no further fuming occurs when air is blown through a glass tube on to the surface of the liquid. D. F. T.

Sulphuric Acid for [Use in] the Nitrate Test. H. D. Steenbergen (*Chem. Weekblad*, 1917, **14**, 647—648).—Sulphuric acid for testing for nitrates in milk can be freed from nitric acid by agitation with mercury in a Lunge nitrometer. A. J. W.

Estimation of Nitrate in the Presence of Chlorides. W. F. Gericke (*J. Ind. Eng. Chem.*, 1917, **9**, 585—586).—In order to avoid the undesirable rise in temperature on the addition of sulphuric acid to the dry mixture of nitrates and chlorides in the colorimetric estimation of nitrates, the author recommends the addition of sulphuric acid and the phenoldisulphonic acid reagent before the evaporation of the solution, the mixture being evaporated subsequently, the temperature of the final stages of the evaporation being preferably below 70°. When the solution has attained the correct concentration as judged by the colour, it is diluted, cautiously neutralised, and compared in the colorimeter with a standard in the usual manner. D. F. T.

The Phenolsulphonic Acid Method for Nitrates in Waters High in Magnesium Salts. M. Starr Nichols (*J. Ind. Eng. Chem.*, 1917, **9**, 586—587).—In the estimation of nitrates by the above process the presence of iron and magnesium salts may cause complications by the formation of a precipitate on the addition of the alkali hydroxide. The author therefore advises the filtration of the solution before the colour comparison if iron is present, but in the absence of iron salts it is sufficient after the neutralisation to add the requisite quantity of ammonium chloride to maintain the magnesium hydroxide in solution, the dilution being effected subsequently. D. F. T.

A New Method for the Destruction of Tissues for the Detection of Arsenic and the Examination of their Ashes. Armand Gautier and P. Clausmann (*Compt. rend.*, 1917, **165**, 11—16).—The tissues or organs are heated in an oven at 300° until they become friable, when they are ground up and mixed with 2—3% of their weight of calcium oxide, which is then slaked with a little water. The mixture is heated in a flat porcelain dish in a furnace at a temperature such that the base of the muffle shows a dull red. At the end of two hours the white, porous ashes are powdered, extracted with water, and acidified with a few drops of sulphuric acid. The mixture is boiled and filtered, the filtrate being evaporated until white fumes appear. The residue is taken up with water and transferred to a Marsh's apparatus, in which the usual estimation of arsenic is made. The results obtained are accurate to 0·001 mg. of arsenic in 100 grams of tissue. The ash could also be used for the detection of borates, silicates, phosphates, fluorine, nickel, silver, or copper. W. G.

A Rapid Method for the Estimation of Water-soluble Arsenic in Lead Arsenate. H. A. SCHOLZ and P. J. WALDSTEIN (*J. Ind. Eng. Chem.*, 1917, **9**, 682—683).—A description of a method closely similar to that of Gray and Christie (this vol., ii, 102), which the authors have used satisfactorily for three years. D. F. T.

The Influence of Calcite Inclusions on the Estimation of Organic Carbon in Soils. EDMUND C. SHOREY and WM. H. FRY (*J. Ind. Eng. Chem.*, 1917, **9**, 588—589).—Attention is directed to the fact that with soils containing calcite included in quartz grains the copper oxide combustion method for the estimation of organic carbon will give values higher than those obtained by the wet combustion method with sulphuric acid and potassium dichromate because the former will cause the liberation of carbon dioxide from the included calcite by disruption of the grains. The lower values for organic carbon frequently obtained by the wet process may therefore not always be due to the greater accuracy of the copper oxide method of combustion. D. F. T.

Acidosis. II. Estimation of Carbon Dioxide and Carbonates in Solution. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1917, **30**, 347—368).—The method is based on that of Swanson and Hulett (A., 1916, ii, 48), in which, however, after shaking the solution of carbon dioxide in a vacuum, the water, instead of the gas, is removed from the chamber and the volume of liberated carbon dioxide then measured over mercury in a calibrated tube at the top of the same chamber. The apparatus consists essentially of a 50 c.c. pipette with three-way cocks at the top and bottom, and a 1 c.c. scale on the upper stem divided into 0·02 c.c. divisions. The pipette is connected at the bottom with (i) a chamber into which the solution is drawn off after the carbon dioxide has been extracted from it, and (ii) a tube to permit the entrance of mercury and subsequent release of the vacuum and measurement of the extracted carbon dioxide. Corrections for the volume of air dissolved in the solution which enters the apparatus and for that fraction of the total carbon dioxide which remains unextracted because of its solubility in water are calculated, and can be applied by a single factor, which can be read off at once from a table included in the text.

The apparatus is designed especially for the analysis of 1 c.c. samples of blood plasma, but is applicable to aqueous solutions in general, as well as for the estimation of dissolved gases other than carbon dioxide. The entire analysis is performed at the ordinary temperature, requires about three minutes, and without special precautions is capable of accuracy to within 1% of the amount estimated.

A micro-apparatus designed on a similar principle is also

described. With it the carbon dioxide content of 0·2 c.c. of blood plasma can be estimated with an accuracy of 1 volume per cent.
H. W. B.

Use of the van Slyke Carbon Dioxide Apparatus for the Estimation of Total Carbon Dioxide in Sea-water. J. F. McClendon (*J. Biol. Chem.*, 1917, **30**, 259—263).—The author describes the adaptation of the van Slyke apparatus (see preceding abstract) for the estimation of carbon dioxide in sea-water, together with the method for applying the numerous necessary corrections to the results.
H. W. B.

Standardisation of a New Colorimetric Method for the Estimation of the Hydrogen-ion Concentration, Carbon Dioxide Tension, and Carbon Dioxide and Oxygen Content of Sea-water, of Animal Heat, and of Carbon Dioxide of the Air, with a Summary of Similar Data on Hydrogen Carbonate Solutions in General. J. F. McClendon (*J. Biol. Chem.*, 1917, **30**, 265—288. Compare this vol., i, 105, and preceding abstract; McClendon and Magoon, A., 1916, ii, 513).—The author gives a detailed account of the methods for estimating carbon dioxide and hydrogen-ion concentration in various fluids by means of slight modifications of apparatus previously described (*loc. cit.*).
H. W. B.

The Correction Values in the Estimation of Free Carbon Dioxide in Water. L. W. Winkler (*Zeitsch. nahr. Genussm.*, 1917, **33**, 443—446. Compare A., 1915, ii, 795).—As a result of the indication by Tillmans and Heublein (this vol., ii, 332) of certain errors in the author's earlier paper (*loc. cit.*) describing his modification of Trillich's method for the estimation of dissolved carbon dioxide by titrating with sodium carbonate solution, the author has re-determined the values of the correction necessary for the adjustment of the titration result.
D. F. T.

The Chemical Examination of Natural Brines. O. R. Sweeney and James R. Withrow (*J. Ind. Eng. Chem.*, 1917, **9**, 671—675).—A tentative suggestion as to a standard method of procedure for the chemical examination of natural brines. Conditions are suggested for the collecting of the sample, the determination of the amount of deposit formed on æration, the determination of specific gravity, and the estimation of total solids, silica, iron and aluminium, calcium, magnesium, barium and strontium, ammonia, sulphuric acid, sodium and potassium, chlorine and bromine. For bromine a colorimetric method is recommended, based on the liberation of bromine by chlorine and comparison of the carbon tetrachloride extract with a similar extract obtained from a solution of known bromine content.
D. F. T.

The Estimation of Strontium and Lithium in Water. S. D. Averitt (*J. Ind. Eng. Chem.*, 1917, **9**, 584—585).—For the estimation of strontium the author recommends the separation of calcium and strontium together as oxalates, with subsequent weighing as oxides; the mixture is then dissolved in hydrochloric acid, reprecipitated as oxalates, and the proportion of strontium deduced by calculation from the quantity of standard potassium permanganate solution required for oxidation of the oxalic acid in combination with the metals.

For the estimation of lithium also, an indirect method is suggested. The weighed mixture of chlorides of lithium, sodium, and potassium is dissolved in water and the potassium and chlorine are estimated in aliquot fractions; by calculation it is then possible to arrive at the proportion of lithium in the original mixture.

D. F. T.

A New Method of Separating Zinc from Cadmium and the Iodometric Estimation of the Latter. Eric John Ericson (*J. Ind. Eng. Chem.*, 1917, **9**, 671. Compare A., 1913, ii, 624).—In the analysis of spelter it is possible to separate the bulk of the zinc from cadmium by crystallisation as zinc sulphate. The filtrate after the removal of the lead from 19·2 grams of spelter (*loc. cit.*) is evaporated until solid commences to separate, then 50 c.c. of dilute sulphuric acid (1 : 3) are added, and the solution is reduced to a volume of 80—100 c.c. by boiling. After keeping overnight the major part of the zinc has crystallised as sulphate; the combined clear solution and washings are diluted, treated with hydrogen sulphide, and the cadmium is then estimated by any suitable method, the addition of excess of *N*/10-iodine and dilute hydrochloric acid, followed by the titration of the remaining iodine with thiosulphate, being quite satisfactory.

The same principle for removing the bulk of the zinc from cadmium can also be applied in the examination of the cadmium content of zinc ores.

D. F. T.

Estimation of Small Amounts of Mercury in Organic Substances. Svend Lomholt and J. A. Christiansen (*Biochem. Zeitsch.*, 1917, **81**, 356—379).—Details of the following processes are described. I. Destruction of organic matter. In the case of urine this is carried out by potassium permanganate in the presence of sulphuric acid. In the case of fæces and organs, a preliminary destruction with nitric acid is first carried out. II. Precipitation by hydrogen sulphide. A small amount of copper sulphate is first added to increase the bulk of the precipitate. III. Filtration. A special form of filter-funnel is figured and described. IV. Solution of the sulphide in nitric and hydrochloric acids. V. Electrolysis of the solution of the sulphides in acid. The mercury is deposited on a small gold electrode in an electrolysis apparatus, which is figured and described. VI. The weighing of the mercury. The gold electrode, when only small amounts of mercury are present, is weighed on a Nernst microbalance. To obtain successful results, attention must be paid to certain details which are described by the authors. S. B. S.

Use of the Platinised Anode of Glass in the Electrolytic Estimation of Manganese. F. A. GOOCH and MATSUSUKE KOBAYASHI (*Amer. J. Sci.*. 1917, [iv], **44**, 53—56).—Anodes, prepared by painting lead glass tubes with an emulsion of chloroplatinic acid in glycerol and then heating to the softening point of glass, have been used for the electrolytic estimation of manganese in solutions of manganous sulphate. Using a current of about 1·7 amperes and 18·3—10·3 volts with an anode of approximately 25 sq. cm. surface which was rotating 150 times per minute, the whole of the manganese was deposited as dioxide in about two and a-half hours. The manganese dioxide was dissolved in a mixture of sulphuric and sulphurous acids, dried at 450°, and weighed as anhydrous manganous sulphate. The method appears to give very accurate results. Some experiments, made to ascertain the influence of certain reagents on the electrolysis, are also described. Thus, when to an electrolyte containing 0·1 gram of manganese per 100 c.c., 5 c.c. of acetic acid and 0·5 gram of chrome alum are added, the complete deposition of the hydrated dioxide required two and a-half hours. If instead of these substances 5 c.c. of alcohol and 2 grams of ammonium sulphate are used, the electrolysis requires three and a-half hours. J. F. S.

Electrolytic Valuation of Iron Sulphide. HOWELL WILLIAMS (*Chem. News*, 1917, **116**, 13—14).—One gram of the finely divided sample is placed along with 5 grams of pure zinc in a 500 c.c. flask and treated with 100 c.c. of dilute hydrochloric acid (D 1·1). The hydrogen sulphide evolved is led into two Fresenius flasks, each containing 50 c.c. of a solution of cadmium chloride (100 grams per litre). A safety flask containing 25 c.c. of the same solution is attached to the end of the apparatus. When the whole of the hydrogen sulphide has been absorbed, the precipitated cadmium sulphide is collected and washed with warm water. The precipitate is then transferred to a 500 c.c. beaker and dissolved in dilute hydrochloric acid. The cadmium is precipitated by a slight excess of sodium hydroxide and the hydroxide redissolved by the addition of a concentrated solution of potassium cyanide. The solution is now diluted to 120 c.c. and electrolysed by a current of 5 amperes and an *E.M.F.* of 5·5 volts, a rotating cathode being employed. The electrolysis is generally complete in ninety minutes. The results obtained are slightly low, approximating in carefully conducted test experiments to about 0·5% below the theoretical value. J. F. S.

Rapid Method for Estimating Nickel and Cobalt in Ores and Alloys. I. W. R. SCHOELLER and A. R. POWELL (*Analyst*, 1917, **42**, 189—199. Compare A., 1916, ii, 346).—Nickel and cobalt are practically quantitatively precipitated as hexamminenickelous iodide, $[Ni(NH_3)_6]I_2$, and hexamminecobaltous iodide, $[Co(NH_3)_6]I_2$, respectively, by an excess of potassium iodide sufficient to give a 4% solution of the precipitant, and in presence of ammonia (D 0·880) in sufficient quantity to form at least two-thirds of the total bulk of the solution. Owing to the slight solubility, very small quantities fail to precipitate within 10—15 mins., but although the reagent is not suitable for estimating traces of nickel and cobalt, results of considerable accuracy, checked against electrolytic and other estimations, were obtained by the application of the method to the assay of ores and alloys. The behaviour of other metals towards potassium iodide and ammonia was studied in numerous cases. Iron and other tervalent metals in presence of excess of tartaric acid are not precipitated, but bivalent iron gives a white precipitate of hexammine ferrous iodide. Manganese and copper are either completely or partly precipitated, but may be easily removed from the precipitate subsequently, the copper as cuprous iodide when the precipitate is treated with hydrochloric acid, and the manganese by reprecipitation of the nickel and cobalt with hydrogen sulphide in presence of acetic acid. It was found advisable to remove alkaline earth metals by preliminary treatment with sulphuric acid. The same applies to lead, but since lead iodide is soluble in ammoniacal tartrate solution, this step is not absolutely necessary. Magnesium and arsenic are without influence on the assay unless present together, when they would interfere owing to precipitation of magnesium ammonium arsenate. Sulphur is oxidised to sulphate and presents no real objection unless a large excess is present, when potassium sulphate might crystallise out from the ammoniacal liquor on addition of the potassium iodide. Excess of hydrochloric acid is to be avoided, as the iodide precipitates are slightly soluble in ammonium chloride.

In carrying out the separation, the precipitates must be washed with a solution containing 800 c.c. of strong ammonia and 40 grams of potassium iodide per litre, as water causes decomposition into basic salts. The washed precipitate is then dissolved in hydrochloric acid with a little sulphurous acid, and after filtration the cobalt is precipitated as cobalt ammonium phosphate and the nickel in the filtrate titrated with cyanide.

Details of the methods adopted with a number of typical alloys and ores, together with the results obtained by various methods, are given in the paper. G. F. M.

[Estimation of Tin in Tin-plate.] I. M. Kolthoff and L. B. van Lohuizen (*Pharm. Weekblad*, 1917, **54**, 718—720).—To estimate tin in scrap tin-plate, a cross-section sample of 50 grams is oxidised by nitric acid to stannic oxide. A portion of the product is reduced to metal in a Rose crucible by hydrogen, the tin dissolved in hydrochloric acid, and estimated by iodine.

A. J. W.

Phosphor-tin and a Volumetric Method for its Analysis. RICHARD EDWIN LEE, W. H. FEGELY, and FRANK H. REICHEL (*J. Ind. Eng. Chem.*, 1917, **9**, 663—668).—A record of the development of a method for the analysis of the alloy phosphor-tin. The procedure adopted is to dissolve the alloy in hydrochloric acid in the first of a series of flasks from which the air has been expelled by a current of coal gas or carbon dioxide. The phosphorus is liberated as phosphine, which is absorbed in the next three flasks by potassium permanganate solution acidified with nitric acid, the phosphoric acid produced being then precipitated as phosphomolybdate; the precipitate is dissolved in aqueous ammonia and the solution titrated with *N*/10-potassium permanganate after reduction by means of a Jones reductor.

The stannous chloride resulting from the action of the hydrochloric acid on the phosphor-tin is estimated by the addition of an excess of ferric chloride followed by titration of the ferrous iron produced with a standard solution of potassium dichromate.

D. F. T.

Estimation of Naphthalene [in Coal Gas] by Picric Acid. KNUBLAUCH (*J. Gasbeleucht.*, 1916, Oct. 14th and 21st; from *J. Soc. Chem. Ind.*, 1917, **36**, 702).—Details are given of a method for estimating naphthalene by passing sufficient of the gas to yield approximately 0·08 gram naphthalene through two wash-bottles containing a 1% solution of picric acid; if the gas contains much ammonia, the picric acid solution for the first wash-bottle is mixed with an equal bulk of sulphuric acid slightly above *N*/2-concentration. The precipitated naphthalene picrate is removed by filtration, washed with a 0·2% solution of picric acid, and finally titrated with *N*/10-alkali and methyl-orange, a correction being made for the picric acid solution absorbed by the filter paper.

D. F. T.

Estimation of Nitrotoluenes. E. KNECHT (*J. Soc. Chem. Ind.*, 1917, **36**, 694).—A reply to Colver and Prideaux (this vol., ii, 340) reasserting that titanous chloride is a convenient reagent for the accurate estimation of aromatic nitro-compounds.

D. F. T.

Estimation of Phenol in Crude Carbolic Acid and Tar Oils. JOHN MORRIS WEISS and C. R. DOWNS (*J. Ind. Eng. Chem.*, 1917, **9**, 569—580).—A detailed description of a method for the accurate estimation of phenol in mixtures with cresols, higher phenols, and neutral oils. In order to obtain satisfactory results, it is necessary that the prescribed directions should be followed closely. The following is a brief summary of the process.

The tar acids are removed from the oil (sufficient to yield approximately 300—350 grams of tar acids) by repeated extraction with 100 c.c. of 20% sodium hydroxide solution, the oil having been previously distilled if dirty. After five extractions with

100 c.c. of benzene, the alkaline solution is rendered slightly acid with sulphuric acid; after settling, the aqueous layer is drawn off and is extracted thrice with 100 c.c. of benzene; phenols are then removed from this by treatment three times with 25 c.c. of 20% sodium hydroxide solution, and, after liberation by the addition of acid, are added to the main bulk of tar acids, the combined weight giving the quantity of wet, crude acids from the tar taken. This yield of acids is then distilled under specified conditions, and fractions are collected up to 190° and between 190° and 202°, the latter fraction being then redistilled and the portion passing over below 197° is added to the distillate obtained up to 190°. This combined distillate is weighed, and further tested as to its solidifying point and specific gravity, the percentage of phenol present being then calculated from a set of curves. In some cases it may be necessary to mix the combined distillate up to 197° with a known proportion of pure phenol before the specific gravity and solidifying point allow definite readings from the curves.

D. F. T.

Direct Polarisation of Sugar Solutions without a Preliminary Treatment with Basic Lead Acetate or the Normal Acetate. H. Pellet (*Bull. Assoc. chim. Sucr. Dist.*, 1916, **35**, 138—140).—The juices from the second carbonation, the sulphited juices, and the syrup solutions in the beet-sugar industry are generally but little coloured. These need not be defecated, but can be polarised directly after clarification by simple filtration with or without the use of kieselguhr.

W. G.

Fehling's Solution in the Estimation of Blood-sugar. H. McGuigan (*Journ. Lab. Clin. Med.*, 1917, **2**, 514—516; from *Physiol. Abstr.*, 1917, **2**, 248).—The danger of utilising a too strongly alkaline Fehling's solution in the determination of blood-sugar is pointed out. Low results are due to the incomplete precipitation of the copper in such cases. The best results are obtained by making the solutions as follows: (1) 34·65 grams of copper sulphate in 1 litre of distilled water; (2) 173 grams of Rochelle salt and 125 grams of sodium hydroxide, made up to 1 litre.

G. B.

Composition of Menhaden Oil Fatty Acids. E. Twitchell (*J. Ind. Eng. Chem.*, 1917, **9**, 581—584).—In order to test the applicability of his m. p. method for the determination of the composition of mixtures of fatty acids (A., 1914, ii, 685), the author has investigated the constituents of menhaden oil. The principle on which the procedure is based is that the m. p. of any pure fatty acid will be lowered by the addition of a mixture of other fatty acids, but that any quantity of the first acid present in the mixture will not contribute to the depression. Using a mixture of 80 parts of a pure acid with 20 of another or of a mixture of others, the average depression is approximately 4°.

In the present investigation, the amount of this depression was directly determined for myristic acid and arachidic acid, the m. p.'s of which were then examined after the addition of the usual proportion of hydrogenated menhaden oil and of the solid fatty acids separated from menhaden oil. The results show that myristic acid is present both in the hydrogenated and in the original oil, but that arachidic acid, although a constituent of the acid mixture from hydrogenated menhaden oil, is not present in the original oil. Arachidic acid therefore must be formed by the reduction of an unsaturated acid in menhaden oil. As a result of this and the previous investigation (*loc. cit.*), the mixture of fatty acids from menhaden oil includes palmitic acid, 22·7%; myristic acid, 9·2%; stearic acid, 1·8%; unsaturated C_{18} acids, 24·9%; unsaturated C_{20} acids, 22·2%; unsaturated C_{22} acids, 20·2%. D. F. T.

The Estimation of Hydroxy-fatty Acids. F. Hodes (*Chem. Zeit.*, 1917, **41**, 492).—In the analysis of fats and oils, it is customary to extract the fatty acids with ether or light petroleum, but under these conditions hydroxy-acids may remain undissolved. For the purpose of dissolving these, a boiling mixture of equal volumes of chloroform and alcohol (96—100%) is advised instead of the absolute alcohol commonly recommended.

D. F. T.

Citric Acid and Tartaric Acid. T. C. N. Broeksmit (*Pharm. Weekblad*, 1917, **54**, 686—687).—Citric acid and malic acid are oxidised by a solution of potassium permanganate in acetic acid to acetone, which can be identified by the iodoform test. The two acids can be distinguished by the fact that barium citrate can be crystallised.

The acetone reaction is applicable to the detection of citric acid in tartaric acid and in lemonade syrup. The presence of tartaric acid in citric acid and in lemonade syrup can be proved by the formation of potassium hydrogen tartrate. A. J. W.

Quantitative Test for Uric Acid in Urine. A. Angiolani (*Policlinico*, 1917, **24**, 415; from *Physiol. Abstr.*, 1917, **2**, 266).—Two hundred and fifty c.c. of urine are mixed with 10 c.c. of concentrated hydrochloric acid and kept for twenty-four hours. The crystals are filtered off, dissolved in 20 to 25 c.c. of 10% potassium hydroxide, acidified with sulphuric acid, and titrated with permanganate. G. B.

Estimation of Unsaponifiable Matter in Oils, Fats, and Waxes. John M. Wilkie (*Analyst*, 1917, **42**, 200—202).—To obviate certain difficulties in the estimation of unsaponifiable matter in oils, etc., such as emulsification during the extraction with ether, the following procedure is recommended: 5 grams of the sample are saponified with 12·5 c.c. of $2N$-absolute alcoholic potassium hydroxide, transferred to a separator with 50 c.c. of water so as to give a concentration of about 20% by volume of alcohol, and extracted successively with 40, 30, and 30 c.c. of ether. Separation is rapid, and the united ethereal extracts are run into a separator containing 20 c.c. of water, which without shaking is first run off before washing the ethereal solution by shaking vigorously with 2, 5, and 30 c.c. of water. The washed extract is evaporated and weighed. The unsaponifiable matter in waxes being but sparingly soluble in ether, it is recommended that only 0·5 gram be taken and mixed with 4·5 grams of castor oil. The above operation is carried out on the mixture, using, however, only 40 c.c. of water at 30° to dilute the alcoholic solution and extracting with 50, 40, 40, and 30 c.c. of ether. A correction is then applied for the known unsaponifiable content of the castor oil. G. F. M.

Estimation of Formalin. G. A. Stutterheim (*Pharm. Weekblad.*, 1917, **54**, 716—717).—Formalin can be estimated by determining the refractive index of the solution. The values of this constant for whole number percentages from 1 to 35 at 17—18° are given, the mean increase for each per cent. being 0·00111. A. J. W.

The Practical Methods for the Detection and Estimation of "Saccharin" in Foodstuffs. A. Bonis (*Ann. Falsif.*, 1917, **10**, 210—218).—A résumé of the literature on the extraction, purification, identification, and estimation of "saccharin." W. G.

Comparative Examination of the Methods Proposed for the Estimation of the Glycyrrhizin in Liquorice Root and in Succus Liquiritiæ. Armin Linz (*Arch. Pharm.*, 1916, **254**, 65—134, 204—224).—All methods recorded from 1800 to about 1880 deal mainly with the isolation of the substance characteristic of liquorice root and Spanish liquorice, and have little or no quantitative value. Subsequently to this date, many investigators, following Rump's lead, proposed different methods for the estimation of glycyrrhizin, the amount of this substance being regarded as a criterion of the quality of a liquorice. It is only within the last ten years that the importance has been emphasised, rightly, of also estimating the amount of sugar, in order that adulteration of a liquorice with sugar may be detected.

Since the amount of glycyrrhizic acid varies between wide limits, not only in different kinds of liquorice, but even in one and the same kind at different times, the author has used always the same liquorice throughout his series of comparative experiments on the trustworthiness of the twenty-seven methods proposed for the estimation of glycyrrhizic acid. In any method, attention must be given to the following points: (1) the influence of the liquid employed as a solvent of the liquorice; (2) the nature of the acid used as the precipitant; (3) the solubility of glycyrrhizic acid in water and in the precipitant, and the loss caused thereby; and (4) the purity of the glycyrrhizic acid when brought to the stage of weighing. All the methods are criticised from these four points of view, and the author draws the conclusion that no one of them is really trustworthy, mainly on account of the impossibility of isolating the glycyrrhizic acid in a pure state. Details are given of a method proposed by the author, which, although tedious and not strictly trustworthy, is less inaccurate than any other previously brought forward.

A tabulated list of the literature on the subject from 1808 to 1913 is given, together with a classified list of the results obtained by the twenty-eight methods discussed in the paper. C. S.

Exact Estimation of Atropine. H. Baggesgaard Rasmussen (*Ber. Deut. Pharm. Ges.*, 1917, **27**, 193—201).—The precipitation of the sparingly soluble salt, $4C_{17}H_{23}O_3N,SiO_2,12WO_3,2H_2O,4H_2O$, by the addition of a slight excess of silicotungstic acid to an acid solution of atropine or its isomerides is made the basis of a quantitative estimation. The belladonna, leaves or extract, is treated with ammonia and ether, and the alkaloids in the ethereal extract are transferred to aqueous solution as hydrochlorides, and precipitated by the addition of silicotungstic acid in about 10% excess. After keeping eight hours, the precipitate is collected on a Gooch crucible, washed with 1% hydrochloric acid, ignited, and weighed. The weight of the inorganic residue multiplied by 0·4067 gives the weight of atropine, to which a correction of 0·0054 gram must be added for every 100 c.c. of the solution in which the precipitation took place. Although the weight of the precipitated salt does not bear an absolutely constant ratio to that of the ignited residue, its nitrogen content is found to do so within the limits of experimental error, from which it is concluded that only atropine or its isomerides are precipitated in the silicotungstate and subsequently estimated. G. F. M.

The Estimation of Nicotine in Tobacco Extract. Th. Sv. Thomsen (*Chem. Zeit.*, 1917, **41**, 476).—Evidence is adduced indicating that the method of Kissling is more trustworthy than that of Ulex for the estimation of nicotine in tobacco extract. The two possible errors in the latter method, viz., the loss of nicotine before distillation and the formation of ammonia during distillation, are not necessarily of equal dimensions, and the production of ammonia may be much more than equivalent to the loss of nicotine, so that the titration of the distillate may give rise to high results. D. F. T.

The Estimation and Nature of Urochromogen. Moriz Weiss (*Biochem. Zeitsch.*, 1917, **81**, 342—355).—Urochromogen can be estimated in urine by two methods. Either the urochrome can be formed by oxidation by permanganate and the amount thus produced can be estimated colorimetrically, or the amount of *N*/100-permanganate necessary to produce the maximal amount of urochrome can be determined by a method described in detail by the author. Pauly's reaction with diazobenzenesulphonic acid in alkaline solution has been applied by the author with Sobolev to the quantitative estimation of histidine (A., 1914, ii, 155). It is shown, however, that the reaction when given by urine is not due to histidine alone, but chiefly to the proteic acid fraction. Urochromogen also gives the reaction, but experiments are quoted which indicate that it is not to this substance in the urine to which the reaction is mainly due. The view is expressed that urochromogen contains a pyrrole nucleus. S. B. S.

The Detection of Blood in Urine, Fæcal Matters, and Pathological Fluids. THEVENON and ROLLAND (*J. Pharm. Chim.*, 1917, [vii], **16**, 18—19).—To 3—4 c.c. of the urine an equal volume of a 5% alcoholic solution of pyramidone is added and 6—8 drops of dilute acetic acid (1 in 3). The mixture is shaken and 5—6 drops of hydrogen peroxide (12 vols.) are added. According to the amount of blood present, an intense violet or bluish-violet coloration develops more or less rapidly. Fæcal matter is triturated with water and filtered, and the filtrate used for the test. This reagent is just as sensitive as Meyer's reagent. W. G.

Simplified Preparation of the Reagent with Phenolphthalein for the Detection of Blood in Urines. ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1917, [vii], **16**, 20).—Meyer's reagent is more simply prepared by using sodium hyposulphite instead of powdered zinc as a reducing agent. Phenolphthalein (2 grams), potassium hydroxide (20 grams), and water (120 c.c.) are warmed together, and to the hot mixture 3 grams of sodium hyposulphite are added. The whole is boiled until the liquid is colourless, when it is allowed to cool, and is then ready for use. W. G.

General and Physical Chemistry.

The Relation between Density and Optical Refraction. V. ROSICKÝ (*Zeitsch. Kryst. Min.*, 1914, **54**, 189; from *Rozpravy české Akademie, Prague*, 1911, **20**, No. 5, 8 pp.).—A new method is proposed for inquiring into the relationship between the densities of crystals and their principal refractive indices. The method consists in comparing the values of the expressions F/d, R/d, where F and R are the volumes of the Fresnel ellipsoid and the optical indicatrix respectively, d being the density. It appears that, in isomorphous and symmorphous groups, R/d remains fairly constant, whilst F/d decreases with increasing molecular weight. The morphological difference between anhydrite and the barytes group is accompanied by a corresponding difference in the values of R/d. In the case of polymorphous substances, the values of R/d and F/d for the different modifications are closely related, the value of the latter expression diminishing with increasing density.

E. H. R.

Phenomena Relating to the Spectra of Hydrogen and Helium. T. R. MERTON and J. W. NICHOLSON (*Phil. Trans.*, 1917, *A*, **217**, 237—278).—The spectra of hydrogen and helium have been examined with a view to the determination of the relative intensities of the lines under different conditions of excitation.

The method employed is essentially the same as that which has been previously used (compare A., 1916, ii, 461) in the determination of the distribution of intensity in broadened spectral lines, and involves the use of a neutral-tinted glass wedge cemented to a similar wedge of colourless glass so as to form a plane-parallel plate. The spectra are photographed through this plate, which is placed in front of the slit of the spectrograph. The photographs obtained under these conditions consist of lines which are dark along the edge corresponding with the thin end of the neutral-tinted wedge and fade away towards the region which corresponds with the thicker end of the wedge. The lengths of the lines on the plate thus correspond with their intensities, and the measurement of these lengths has been accomplished by preparing positives from the negatives and enlarging these on to bromide paper through a ruled "process" screen. By this means an enlarged negative is obtained, in which the lines are made up of minute dots, and the length of any line can be determined by the position of the last visible dot. By the use of this "process" screen, personal error is almost entirely eliminated.

It is shown, further, that the intensities determined by the above method can be expressed in terms of the intensity of the continuous black body radiation from the positive crater of the carbon arc.

The results obtained show that the distribution of intensity in the lines belonging to a particular series varies with the conditions of discharge. Under conditions in which there is a transfer of energy from the longer to the shorter wave-lengths in a given series it is found that the associated series, in particular the diffuse series, are relatively enhanced at the expense of the principal series. It has also been found that the distribution of intensity observed in certain celestial spectra can be approximately reproduced in the laboratory.

The question of the relative behaviour of hydrogen and helium cannot be satisfactorily discussed until the nature of the Balmer series is established. According to Sommerfeld, the Balmer series represents effectively a supposition of diffuse, sharp, and principal series, but the authors' measurements of the separation of the doublets constituting the lines H_α and H_β afford no support for this view. The measured separations are 0·132 Å. and 0·033 Å. respectively, and it is pointed out that these values are consistent with the hypothesis that the lines in question are principal series lines. The separation in the case of H_α is in precise agreement with the value deduced by Buisson and Fabry. H. M. D.

Wave-lengths of the Stronger Lines in the Helium Spectrum. Paul W. Merrill (*Chem. News*, 1917, **116**, 130—133).—The wave-lengths of twenty-one of the stronger helium lines have been measured by using a Fabry-Perot interferometer. In nine cases the wave-lengths were compared directly with that of the standard cadmium line by photographing the two spectra simultaneously on the same plate. The estimated error in the measurements is less than 0·003 Å.

In regard to the representation of the helium series by a three-constant formula of the type $n = A - B/m^2 - C/m^3$, in which n is the frequency, m a series of successive integers, and A, B, and C are constants, it is shown that the formula based on the measurements of lines for which $m = 3$, 4, and 5 in each of the six series, does not reproduce accurately the frequency of even the next number ($m = 6$) in any one of the series. In every instance the divergence between the observed and calculated values is greater than the error of experiment, whilst the residuals show a fairly smooth and converging increase towards the terms of higher order. H. M. D.

The First Electron Ring of the Atoms. P. Debye (*Physikal. Zeitsch.*, 1917, **18**, 276—284).—According to Bohr's theory, the K series of lines in the high frequency spectra is attributable to the innermost ring of electrons. The frequencies of the α lines of the K series in the spectra of the elements between sodium (atomic number 11) and neodymium (atomic number 60) are considered in reference to Sommerfeld's formula, and it is suggested that the applicability of this formula to the K series of lines can be satisfactorily explained on the assumption that the innermost ring of electrons in the atoms of all elements, with the exception of those of low atomic number, consists of three electrons.

H. M. D.

Absorption Spectra and Chemical Constitution of Organic Compounds. J. J. DOBBIE, E. C. C. BALY, and A. W. STEWART (*Brit. Assoc. Rep.*, 1916, 131—186).—An alphabetical list of all organic compounds the absorption spectra of which have been measured in the infra-red, visible, and ultra-violet regions of the spectrum, with references in each case. C. H. D.

The Chromophore Function. I. LIFSCHITZ (*Zeitsch. wiss. Photochem.*, 1916, **16**, 140—152. Compare this vol., ii, 62).—As a qualitative method for the investigation of the absorption, the Hartley-Baly method has been found to be very convenient, and it is shown that the observations made according to this mode of procedure may be utilised in the determination of the magnitude of the extinction-coefficient for light of different wave-lengths. The values obtained in this way are found to be in satisfactory agreement with the extinction-coefficients afforded by direct measurement.

The question of the possibility of calculating the absorption of a compound from constants characteristic of certain groups is discussed, and theoretical arguments are advanced against the view that this is feasible. H. M. D.

The Influence of Constitution on the Rotation of Optically Active Substances. IX. Absorption Spectra of some Compounds with "Relatively Abnormal" Rotation-Dispersion. H. RUPE and L. SILBERSTROM (*Annalen*, 1917, **414**, 99—111).—A suggestion put forward by Tschugaev (A., 1911, ii, 450) to the effect that anomalous rotation-dispersion is connected with selective absorption in the ultra-violet, in the neighbourhood of the visible spectrum, has been investigated in the case of some dienes obtained by the action of Grignard agents on citronellaldehyde, some menthyl and myrtenyl esters, and some camphor derivatives. No such connexion has been established in these cases, for no substance examined has a selective absorption, although many have "relatively abnormal" rotation-dispersion (compare A., 1915, ii, 717; A., 1914, i, 131), verging in the case of diphenylmethylenecamphor into the really anomalous. Curves connecting wave-lengths with the logarithms of the layer thicknesses in millimetres are reproduced.

The preparation of diphenylmethylenecamphor and diphenylcamphorylmethane is described (compare Haller and Bauer, A., 1906, i, 441). The present authors find somewhat different constants for these compounds: diphenylmethylenecamphor has m. p. 113·5°, $[\alpha]_D^{20}$ +242·99°, in 10% benzene solution (Haller and Bauer found m. p. 113·5°, $[\alpha]_D$ +287° in alcohol); diphenylcamphorylmethane has b. p. 225°/12 mm., m. p. 135·5—136·5°, $[\alpha]_D^{20}$ +19·87°, 19·32°, in 10% benzene solution (Haller and Bauer found m. p. 106—107°, and $[\alpha]_D$ varying from +40°29′ to 80°10′). It is proposed, therefore, to investigate compounds of these types more thoroughly. J. C. W.

Production of Light at Low Temperatures by Catalysis with Metal and Metallic Oxide Hydrosols. B. C. Goss (*J. Biol. Chem.*, 1917, **31**, 271—279).—When a solution of pyrogallol is mixed with hydrogen peroxide in the presence of certain colloidal metal and metallic oxide sols, oxidation occurs rapidly with the production of white light. Visible light is produced in the presence of concentrations of colloidal platinum as low as 1 part in 250,000, whilst with higher concentrations similar effects are observed even when the temperature of the solutions is below zero. Gelatin, egg-albumin, and other protective colloids inhibit the production of light, whilst potassium stearate and amyl alcohol markedly increase it. The action of the colloidal metal is similar to that of the plant oxydases (Harvey, *Amer. J. Physiol.*, 1916, **41**, 454), except that in the former case the catalyst is not destroyed. The catalysis is apparently not due entirely to the high degree of dispersion of the metal or oxide and the consequent large specific surface, but is also dependent on the ability of the metal to form unstable compounds with oxygen. The phenomenon closely resembles that observed in luminous organisms. H. W. B.

Bioluminescence. VIII. Mechanism of the Production of Light during the Oxidation of Pyrogallol. E. Newton Harvey (*J. Biol. Chem.*, 1917, **31**, 311—336. Compare this vol., i, 365, and Goss, preceding abstract).—In addition to the substances already recorded, chromates, dichromates, hypochlorites, hypobromites, hypoiodites, chromium and iron salts, colloidal silver, oxides of manganese, metallic silver, and silver oxide all produce light when mixed under certain conditions with pyrogallol and hydrogen peroxide. Ferrocyanide solutions only give a bright light with pyrogallol and hydrogen peroxide after exposure to sunlight and air, due, apparently, to the formation by *photochemical* action of a substance in the ferrocyanide which is able to effect the rapid transfer of oxygen from the hydrogen peroxide to the pyrogallol. Perborates, persulphates, sodium and barium peroxides may replace hydrogen peroxide without inhibition of light production in the presence of some of the above oxidising agents, but not of others. The presence of a peroxide is not always absolutely essential; pyrogallol mixed with sodium hypochlorite or hypobromite, with ozone, or with acid (but not neutral or alkaline) permanganate, is rapidly oxidised with the evolution of visible light. Alkali sometimes favours luminescent oxidation and sometimes inhibits it; the action of acid also varies according to the oxidising agent present.

The effects of variation of the concentration and of temperature on light production during the oxidation of pyrogallol by potassium ferrocyanide in the presence of hydrogen peroxide have been ascertained. There is an optimum concentration of pyrogallol and of ferrocyanide at which the intensity of the light produced is a maximum. Increase of temperature also increases the brightness of the light up to an optimum temperature; then a decrease occurs. The greater the concentration of the reacting solutions, the higher the optimum temperature for maximum light production. Light is also produced when the oxidation of the pyrogallol occurs in 50% alcohol or acetone. H. W. B.

Interference Effects of Irregularly Orientated Particles in Röntgen Light. III. The Constitution of Graphite and Amorphous Carbon. P. DEBYE and P. SCHERRER (*Physikal. Zeitsch.*, 1917, **18**, 291—301).—The methods introduced by von Laue and by Bragg for the investigation of crystal structure require well-formed crystals and also a knowledge of the system to which the crystals under examination belong. In the method which has been described by the authors (compare also *Physikal. Zeitsch.*, 1916, **17**, 277), it is unnecessary to have any information relative to the crystallographic system, and the investigation of the structure can be effected on crystals of microscopic or even submicroscopic dimensions. The interference figures are obtained by pressing the crystalline powder to form a small rod, which is placed in the axis of a cylindrically arranged sensitive film and subjected to the influence of monochromatic Röntgen radiation, when characteristic curves are produced on the film as a result of the interference phenomena which are conditioned by the characteristic structure of the minute crystals.

This method has been applied in the investigation of the structure of graphite and amorphous carbon. The crystallographic data for graphite in the literature are quite contradictory, and the fact that the system to which graphite belongs has not previously been fixed with certainty is entirely due to the lack of well-formed crystals of sufficient size. The interference curves show clearly that graphite is trigonal, and the arrangement of the carbon atoms follows from the nature of these curves.

By subjecting amorphous carbon to examination in similar manner, interference figures are obtained which suggest that this amorphous variety is identical in structure with graphite, and that it only differs from graphite by its greater degree of subdivision.

The authors thus conclude that diamond and graphite are the only two known modifications of carbon. In the former the carbon valencies are arranged tetrahedrally, whilst in graphite the carbon atom appears to have its three principal valencies in one plane inclined to another at 120°, whilst the fourth valency (secondary) is disposed at right angles to this plane. This is said to correspond with the difference in chemical behaviour. H. M. D.

Separation of Isotopes. FREDERICK SODDY (*J. Amer. Chem. Soc.*, 1917, **39**, 1614—1615).—A criticism of a recent statement by Richards and Hall (this vol., ii, 230) of the existing position of the evidence on which is based the view that isotopes are not separable by chemical means. This view is not to be judged by a particular line of evidence, whether this is the proof that each radio-element has an isotope to which it is more closely allied than to any of the other elements, or the non-separability by the frequent repetition of the same operation on the same pair or by the application of all the available methods to the same pair, but by the agreement of the results which are afforded by all three methods of investigation. H. M. D.

Periodicity among the Radioactive Elements. NORRIS FOLGER HALL (*J. Amer. Chem. Soc.*, 1917, **39**, 1616—1619).—By reference to the elements with atomic numbers 81 to 92, it is pointed out that the number of known isotopes in a pleiad and the character of the predominant radiation show a periodic variation of the type to be expected on the hypothesis that the atoms are built up from hydrogen and helium. This periodicity of two has already been noted by Harkins in the variation in the abundance and the atomic weight of the lighter elements and in the stability of the heavier elements. In so far as isotopic complexity and predominant radiation are concerned, it appears that the isotopes of even-numbered elements are more numerous than those of odd-numbered elements. The former show a well-marked tendency to undergo disintegration with the emission of α-rays rather than β-rays. This accords with the hypothesis that even-numbered elements belong to the helium system. H. M. D.

The Relative Electrode Potentials of Tin and Lead determined by Equilibrium Measurements with their Perchlorates. ARTHUR A. NOYES and KEBE TOABE (*J. Amer. Chem. Soc.*, 1917, **39**, 1537—1545).—The equilibrium in the system $Sn(solid) + Pb^{\cdot\cdot} = Pb(solid) + Sn^{\cdot\cdot}$ has been examined in a series of experiments in which metallic tin and lead, in the form of very fine shavings, were brought into contact with solutions of the corresponding perchlorates, the mixtures being rotated in stoppered bottles for ten to twenty days at 25° until a condition of equilibrium was attained. The perchlorates of both metals are soluble and are probably normally ionised. For these and other reasons, the perchlorates probably afford more satisfactory material for the investigation of the equilibrium in question than most other salts.

The measurements gave 2·98 as the mean value of the equilibrium ratio Sn/Pb. In previous measurements with chloride solutions, Sackur (A., 1904, ii, 336) found 3·34 to 3·45 for this ratio. The smallness of the difference between the two values suggests that the formation of complexes in the chloride solutions is not very considerable.

Assuming that the tin and lead perchlorates are equally ionised, the value 2·98 represents also the ratio $Sn^{\cdot\cdot}/Pb^{\cdot\cdot}$, and from this the difference between the normal electrode potentials of tin and lead is found to be $E_{Sn} - E_{Pb} = +0{\cdot}0140 \pm 0{\cdot}0001$ volt. According to data in the literature, the normal potential of lead referred to the hydrogen electrode is $+0{\cdot}132$ volt, and therefore the normal potential of tin is $+0{\cdot}146$ volt. It should be noted that the positive sign, which is given to these electrode potentials, is opposite to that which is commonly employed. H. M. D.

Electromotive Behaviour of Lead. PAUL GÜNTHER (*Zeitsch. Elektrochem.*, 1917, **23**, 197—199).—It is shown that lead electrodes capable of yielding sharp potential measurements of lead may be prepared by electrolytically depositing lead on a platinum wire from a 0·1005*N*-solution by a current of 1—2 milliamperes. With this electrode, the combinations $Pb|PbCl_2(sat.)||AgCl|Ag$ and $Pb|PbCl_2(sat.)||Hg_2Cl_2|Hg$ were measured. From the results, the heat change of the reaction $Pb + 2AgCl = PbCl_2 + 2Ag$ is found to be $U_0 = 12{,}195$ cal., and the heat of formation of lead chloride is 85,400 cal. The heat of the reaction $Pb + Hg_2Cl_2 = PbCl_2 + 2Hg$ is $U_0 = 10{,}870$ cal., and the heat of formation of lead chloride 85,380 cal. A number of heats of formation for various lead salts has been calculated from the present measurements. The following values are given: $PbBr_2$, 67,100 cal.; PbI_2, 42,400 cal.; $Pb(NO_3)_2$, 108,100 cal.; $PbSO_4$, 218,800 cal.; $PbCO_3$, 169,500 cal.; PbO, 52,900 cal.; PbS, 20,900 cal.; PbSe, 18,400 cal.; PbTe, 14,000 cal. J. F. S.

The Theory of Electrolytic Ions. VII. Determination of the Constitution of Complex Salts by Mobility and Conductivity. RICHARD LORENZ and I. POSEN (*Zeitsch. anorg. Chem.*, 1916, **95**, 340—352. Compare this vol., ii, 14).—The constitution of complex multivalent salts cannot be determined from determinations of the transport numbers or of the conductivity alone, but may be so from a comparison of transport number and conductivity. These relations are discussed mathematically, with application to the complex salts of cobalt. C. H. D.

Chemical Reactions in Anisotropic Liquids. IV. THE. SVEDBERG. (*Kolloid Zeitsch*, 1917, **21**, 19—21. Compare this vol., ii, 249).—The influence of a magnetic field on the rate of change of the electrical conductivity of solutions of pyrogallol and picric acid in *p*-azoxyphenetole has been investigated under more favourable conditions, rendered possible by the use of a large and powerful electromagnet.

Under the influence of the field, the rate of increase of the conductivity becomes smaller, but the ratio between the rates with and without the magnetic action is independent of the nature of the solute, which is supposed to act as a catalyst, and also of the magnitude of the absolute velocity of reaction as measured by the rate of change of the conductivity. Between 9000 and 3500 gauss, this ratio is also independent of the strength of the field, but has a distinctly greater value for a field of 500 gauss. With rise of temperature, the ratio increases and becomes equal to unity at the clearing temperature. H. M. D.

Homogeneous Equilibrium and Additivity of Internal Atomic Heats ($C_v - 3/2R$) in Ideal Gases. MAX TRAUTZ (*Zeitsch anorg. Chem.*, 1916, **95**, 79—104. Compare A., 1916, ii, 304, 422).—The rule of additivity of internal atomic heats holds good exactly or very approximately in the great majority of cases. Such deviations as are found are irregular. The molecular composition of a gaseous mixture is more uncertain the higher the temperature. The rule of additivity is tested by means of a large number of tables. C. H. D.

Molecular Heat of Zinc Dimethyl Vapour. An Example of the Additive Nature of $C_v-3/2R$. MAX TRAUTZ (*Zeitsch. Elektrochem.*, 1917, **23**, 206—212).—The contradiction, met with between the dissociation of iodine and bromine, with respect to the additive character of the atomic heat, is discussed. It is shown that the integration constant of the bromine dissociation equilibrium differs by 2·7 units from that derived from the additive nature of $C_v-3/2R$. This example shows that even in the case of a fundamentally divergent example a very considerable approximation of the equilibrium may be achieved from the additive nature of $C_v-3/2R$. The molecular heat of zinc dimethyl may be calculated to 12·6 on the basis of strict additivity, whereas the experimentally determined value lies between 12 and 13. The molecular heat of carbon dioxide at the ordinary temperature is found by Kundt's method to be 8·56, a value in agreement with previous measurements and diverging from the value calculated on the basis of additivity. From these results it is stated that the additivity of $C_v-3/2R$ is extremely good in the case of gases of similar character, but is never absolute. J. F. S.

Thermodynamic Contents of Ammonia. I. The Heat Capacity of Liquid Ammonia. FREDERICK G. KEYES and HENRY A. BABCOCK (*J. Amer. Chem. Soc.*, 1917, **39**, 1524—1537).—Measurements of the specific heat of liquid ammonia have been made by a mixture method in which the heat capacity of the ammonia is compared directly with that of water. The comparison is effected by the use of two bombs of the same weight, shape, and heat capacity, the weight of water in the water bomb being adjusted by trial experiments until its heat capacity is identical with that of the ammonia in the ammonia bomb. By this mode of procedure, the water equivalent of the calorimeter is eliminated, and the uncertainty respecting the temperature of the bomb at the instant it passes into the calorimeter is removed by an exactly reproducible method of rapidly transferring the bomb from the thermostat to the calorimeter. A small correction is, however, required for radiation, because of the fact that the rates of equalisation of the temperature in the calorimeter are different for the two substances concerned.

In terms of the specific heat data for water recorded by Bousfield, the measurements give 1·152 for the mean specific heat of liquid ammonia between 0° and 20°, and 1·172 between 20° and 50°. These specific heat values are expressed in 15° calories. Assuming that the true specific heat is a linear function of the temperature, it may be represented by the equation $c=1{\cdot}144+0{\cdot}0008t$. H. M. D.

Use of Shukov's Apparatus for Molecular Weight Determinations. ED. GRAEFE (*Zeitsch. angew. Chem.*, 1917, **30**, i, 44. Compare A., 1916, ii, 123).—The author has used a Shukov apparatus for some years in the determination of molecular weights by the depression of the melting-point method, and has found the apparatus to be quite suitable for the purpose. A vacuum jacket is not essential if the apparatus has double walls. Stearic acid is a useful solvent in many cases. W. P. S.

The Melting Points of Homologous Series. G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1916, 172—176; from *Chem. Zentr.*, 1917, i, 1070).—Aliphatic monocarboxylic acids with an even number of carbon atoms have higher m. p.'s than the preceding or succeeding acids with an odd number of carbon atoms. According to the author, this regularity may be due to the fact that the former occur in two stable, crystalline forms, whilst only one stable form of the latter is known. The equilibrium diagrams show the probability of this hypothesis at any rate for the first two members of the series, formic and acetic acids. H. W.

The Guldberg and Trouton-Nernst Rules in Homologous Series of Compounds. W. HERZ (*Zeitsch. anorg. Chem.*, 1916, **95**, 253—256. Compare A., 1916, ii, 311).—The ratio of the absolute boiling point to the critical temperature, which according to Guldberg's rule should be constant and equal to two-thirds, is shown to increase in homologous series with the number of carbon atoms.

Trouton's rule is found to give irregular results when tested in the same way, whilst the values corresponding with Nernst's formula increase with increasing carbon. C. H. D.

Vapour Pressures in the System: Carbon Disulphide–Methyl Alcohol. E. H. BÜCHNER and ADA PRINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1232—1242).—When the vapour, which is in equilibrium with the conjugate solutions formed by a pair of partly miscible liquids, is intermediate in composition with respect to that of the two liquid solutions, it has been assumed that when the temperature reaches the critical solution temperature, the composition of the vapour will be the same as that of the critical solution. Although this view has been shown to be untenable on theoretical grounds, there is no experimental evidence which bears directly on the question. In these circumstances, the authors have investigated the conditions of equilibrium in the system carbon disulphide–methyl alcohol in the neighbourhood of the critical solution temperature 37·3°. The vapour pressures of various mixtures of the two substances at different temperatures are recorded in tables, and the composition of the vapour in equilibrium with the conjugate solutions at certain temperatures is also shown.

From the observations, it is not possible to say whether the composition of the vapour in this particular system remains intermediate to that of the two liquids right up to the critical solution temperature, but this appears to be the case at all temperatures below 35·2°, which is only 2° below the critical temperature.

H. M. D.

Experimental Manipulation. The Manipulation of Small Quantities of Volatile Substances. II. ALFRED STOCK (*Ber.*, 1917, **50**, 989—1008. Compare A., 1914, ii, 171).—A complicated apparatus is described and figured, which is designed for the fractional distillation and determination of the physical constants of small quantities of volatile substances. It embodies all the features of the apparatus designed from time to time by the author in his work on boron, silicon, and carbon compounds (compare A., 1915, ii, 339; this vol., ii, 192, 308). J. C. W.

Determination of Gas Density. J. D. EDWARDS (*J. Ind. Eng. Chem.*, 1917, **9**, 790—792).—A specific gravity balance is mounted in a water-jacketed gas chamber, which is closed by screw-caps and provided with a gas inlet, mercury gauge, and a needle-valve. The balance beam carries at one end a closed globe and at the other a pair of adjustable counterweights. The gas chamber is first filled with air and the pressure adjusted by means of the needle-valve until the beam just balances at a predetermined point. The operation is then repeated with the gas under examination. The specific gravity of the gas is the ratio of the total pressure (gauge plus atmospheric pressure) at which the beam balances in air to the total pressure at which it balances in the gas. W. P. S.

Vacuum-jacketed Pyknometer for Liquids. FRANK HALL (*J. Amer. Chem. Soc.*, 1917, **39**, 1319—1320).—A pyknometer of the type described by Davis and Pratt is modified by the addition of a vacuum jacket. In use the inner portion is washed out two or three times with the liquid the density of which is required, after this liquid has been brought to the desired temperature. The pyknometer fitted in this way does not require to be immersed in a constant temperature bath, and the adjustment of the level in the capillary tube can be made at once. H. M. D.

Influence of Unsaturation on the Molecular Volumes of Solid Compounds. GERVAISE LE BAS (*Chem. News*, 1917, **116**, 97—98).—Examples are given to show that the ethenoid linking of an unsaturated compound causes a contraction which has approximately the same value for a large number of aromatic compounds.

H. M. D.

The Surface Tension of Stereoisomeric Compounds. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **82**, 1—8).—The surface tension of solutions of certain stereoisomerides differed from one another when measured by stalagmometric methods. This was found to be the case with the limonenes (*d*- and *l*-), pinenes (*d*- and *l*-), and mandelic acids (*l*- and *i*-). S. B. S.

Viscosity of Solutions. SVANTE ARRHENIUS (*Bio-Chem. J.*, 1917, **11**, 112—133).—A discussion of recent measurements of the viscosity of solutions and pseudo-solutions, with special reference to Einstein's formula and the empirical logarithmic formula suggested by the author (A., 1888, 336). This leads to the conclusion that Einstein's formula, as applied to colloidal solutions, represents a limiting law which is not in accord with the behaviour of actual solutions, in that for these the viscosity increases with the concentration more rapidly than the law demands. The deviations are attributable to the Brownian motion, to the non-spherical form of the colloidal or suspended particles, and to the formation of aggregates by combination with the solvent. The logarithmic formula has a much larger range of validity, and is applicable to true as well as to pseudo-solutions. Deviations from the logarithmic formula $\log \eta = \theta c$, in which θ is a constant, are brought about by dissociation of the solvent or solute molecules or by association between molecules of the solvent and the solute. Hatschek's objections to the logarithmic formula are criticised adversely. H. M. D.

Adsorption of Sulphuric Acid by Ferric Hydroxide and Formation of Colloidal Sulphur from Sulphides. E. DITTLER (*Kolloid Zeitsch.*, 1917, **21**, 27—28).—Experimental results are recorded which show that sulphuric acid is adsorbed by ferric hydroxide to such an extent that errors may be introduced in the estimation of sulphur in pyrites by Lunge's method.

By the action of steam on pyrites and marcasite for prolonged periods, it has been found that small quantities of colloidal sulphur are produced. It is suggested that native sulphur may in some cases have been formed by a similar action. H. M. D.

Adsorption by Soils. J. E. HARRIS (*J. Physical Chem.*, 1917, **23**, 454—473).—Finely divided dry soil or kaolin has been treated with a number of salt solutions of various concentrations, and the adsorption of the various cations and anions determined. Under this treatment it is shown that the cation adsorption follows very closely the adsorption isotherm represented by the equation $x/m = ac^{1/n}$, indicating that the action is one of pure adsorption and not of double decomposition. The adsorption differs with different salts, the order of adsorption tendency for the cations being $Al^{\cdot\cdot\cdot}$, $K^{\cdot}$, $Ca^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Na^{\cdot}$, the adsorption values for calcium, manganese, and magnesium being almost alike. In the above series it is clear that, with the exception of potassium, the metals follow the order of their valency, and metals of the same valency give practically the same adsorption value. It was found that a soil which had adsorbed large quantities of potassium would give up part of this when treated with various salt solutions. In the case of the solutions used, it was found that they follow the order $AlCl_3$, NH_4Cl, $MnCl_2$, $CaCl_2$, $CaSO_4$, $MgCl_2$, $NaCl$, $CaCO_3$ with respect to their ability to remove adsorbed potassium. When a soil was treated with a solution of a mixture of salts, it was found that the amount of each ion adsorbed was reduced by the presence of the other. The total number of equivalents adsorbed from the mixture was, however, greater than that from either salt alone. J. F. S.

Semipermeable Membranes and Negative Adsorption. WILDER D. BANCROFT (*J. Physical Chem.*, 1917, **21**, 441—453).—A theoretical paper in which semi-permeability and negative adsorption in its connexion with osmosis are discussed. It is shown that osmotic phenomena are exhibited by a porous diaphragm provided that there is a marked negative adsorption and that the diameter of the pores is so small that the adsorbed films practically fill the whole of the pores. A porous diaphragm will act as a semipermeable membrane when there is no measurable adsorption of the solute and when the adsorbed films fill the pores completely. In the usual case of a semipermeable diaphragm there is no porous wall, and the semipermeability is due to the fact that the solvent dissolves in the diaphragm, whilst the solute does not do so, to an appreciable extent, under the usual experimental conditions. A liquid is not to be considered as a porous substance, and solubility does not depend on porosity. J. F. S.

Capillary Phenomena and Supercooling. S. LAWRENCE BIGELOW and EDWARD A. RYKENBOER (*J. Physical Chem.*, 1917, **23**, 474—512).—The temperature of solidification of sulphur, aceto-*o*-toluidide, β-naphthol, acetanilide, oxalic acid, and benzoic acid has been determined in tubes varying in internal diameter from 4·8 mm. to 0·132 mm., with the object of ascertaining whether any relationship could be observed between the diameter of the tube and the amount of supercooling. The measurements were made in a rather complicated sulphuric acid bath fitted with an arrangement for withdrawing the hot acid and leading in cold acid. It is shown that, whilst a mathematical connexion between the diameter of the tube and the amount of supercooling could not be found, a great degree of supercooling is observed in the narrower tubes. The authors offer a theory to explain the phenomena observed. It is shown that the nature of the material of the tube has little, if any, effect on the amount of supercooling, and that small changes of surface tension and changes in the rate of cooling have no influence on the amount of supercooling. In the case of sulphur, it is shown that the amount of supercooling depends on the temperature to which the substance was previously heated. J. F. S.

The Partial Separation by Thermal Diffusion of Gases of equal Molecular Weight. S. CHAPMAN (*Phil. Mag.*, 1917, [vi], **34**, 146—151).—Theoretical reasoning leads to the conclusion that a temperature gradient in a mixture of two gases is sufficient to produce diffusion, independently of any non-uniformity of composition or of the action of external forces. It is now shown that "thermal diffusion" offers a means of partly separating two gases of equal molecular weight provided that the diameters of the two kinds of molecules or the laws of their interaction are not identical. When the diameters are unequal, the larger molecules tend to pass towards the cooler regions. In its application, the method is limited by the approximate agreement of the diameters of many molecules of the same mass. H. M. D.

The Theory of Solution. E. J. HARTUNG (*Trans. Faraday Soc.*, 1916, **12**, 66—84).—The density, heat capacity, and heat change on mixing have been determined for a series of mixtures of selected pairs of liquids. The two liquids are introduced into the thin copper calorimeter, internally silvered, by means of weight pipettes, and stirred with a glass disk stirrer. The deviations of the observed properties from a simple mixture law are plotted by Denison's method (A., 1913, ii, 30), and the solvate explanation is adopted, although the variations in the curves suggest that two or more solvates may be present, and a quantitative verification is not possible. Nitrobenzene and ethyl ether exhibit a very small heat change on mixing, and the heat capacity scarcely deviates from the mixture law, although the contraction on mixing is considerable. The deviation curve is unsymmetrical. For aniline and ethyl ether, the curves for all three properties are similar and unsymmetrical, and do not correspond with any single solvate. For aniline and methyl alcohol, the deviation curves for contraction and heat capacity both pass through a maximum, but are otherwise dissimilar, whilst the heat change curve has both a maximum and a minimum. Aniline and carbon tetrachloride give a large absorption of heat on mixing, and the curves are not quite symmetrical. C. H. D.

Influence of Salts on Solubility. H. VON EULER AND OLOF SVANBERG (*Zeitsch. Elektrochem.*, 1917, **23**, 192—197).—The influence of a number of electrolytes on the solubility of certain non-electrolytes in water has been determined, together with the change in surface tension of the solutions. With regard to the effect of sodium salts of aliphatic acids and inorganic acids, it is shown that the solubility of aniline, nitrobenzene, and ethyl ether in water is reduced, but in the case of sodium salts of aromatic acids, the solubility is increased. The authors show that whilst there is a certain parallelism between the surface tension and the solubility, yet no definite relationship between the two can be formulated. The authors attribute the difficulty of bringing the solubility influence into line with other ionic properties to the fact that the action in the present case is due to two superimposing influences, the one depending on the electrical charge of the ions, which changes the properties of the solution through electrostriction, and the other connected with the chemical nature of the ions, which often acts in the direction opposed to the former action. J. F. S.

Comparative Solubilities in Water, Pyridine, and in Aqueous Pyridine. WILLIAM M. DEHN. *J. Amer. Chem. Soc.*, 1917, **39**, 1399—1404).—The solubilities of some eighty-five miscellaneous compounds in water, pyridine, and a mixture of these in equimolecular proportions are tabulated, most of the data being new. The work was inspired by the discovery that helianthin is vastly more soluble in the mixture than in the pure liquids; 100 grams of water, pyridine, or mixture at 20—25° dissolve 0·02, 1·80, or 51·50 grams of helianthin respectively. It is found that certain other dyes, alkaloids, and nitrogen compounds (fifteen cases in all) share this property, whilst lactose, maltose, and raffinose are less soluble in the mixture than in either solvent. The results are briefly discussed in the light of the accepted views on solubility.

J. C. W.

The Relation between Chemical Constitution and Crystal Structure. P. Groth (*Zeitsch. Kryst. Min.*, 1915, **54**, 498—504).—It has been shown by von Eucken (*ibid.*, 410) that whilst the heat conductivity of crystals increases as the temperature falls, that of amorphous substances, such as glasses, decreases, and, further, that the conductivity of crystalline aggregates is less than that of individual crystals. It follows that heat conductivity is favoured by homogeneity, which in a crystal reaches a maximum at the absolute zero, when the atoms are at rest.

The structure of diamond crystals is in accordance with the quadrivalent character of the carbon atom, and from this it is argued that atoms in general must be regarded as anisotropic. Hence molecules are also anisotropic, in the sense that their properties vary in different directions. As the molecule increases in size, however, the anisotropic character becomes less apparent, and the externally directed forces which lead to crystallisation less strong. This explains why substances with very large molecules, such as the characteristic colloids, do not crystallise.

When a substance crystallises, whilst part of the molecular interatomic forces is transferred to neighbouring molecules, part of them persist in the crystal structure, as is shown by many instances of close relationship between chemical constitution and crystalline form. Such relationships are specially common among aromatic benzene derivatives, the benzene ring structure evidently exerting a determinative influence on the crystalline form. Among aliphatic compounds such relationships are far less common, but recent work has shown that if the chain structure be closed, as in the anhydrides of dibasic acids, to form a ring, the crystal structure is less subject to large variations (compare Stefl, this vol., i, 535). Recent determinations of the densities of maleic acid (1·609) and maleic anhydride (1·509) make it possible to determine the topic parameters of these compounds and to compare them with those of succinic acid and its anhydride:

Succinic acid, $\chi:\psi:\omega = 3{\cdot}413:5{\cdot}940:5{\cdot}097$; $\beta = 133°37'$.
Maleic acid, $\chi:\psi:\omega = 3{\cdot}977:5{\cdot}384:3{\cdot}783$; $\beta = 117°7'$.
Succinic anhydride, $\chi:\psi:\omega = 3{\cdot}711:6{\cdot}242:2{\cdot}873$; $\beta = 90°0'$.
Maleic anhydride, $\chi:\psi:\omega = 3{\cdot}814:5{\cdot}952:2{\cdot}854$; $\beta = 90°0'$.

The parameters of the anhydrides are much more closely related than those of the acids. Further investigations of aliphatic compounds with closed structures are suggested. E. H. R.

Crystal Structure. I. & II. A. Schoenflies (*Zeitsch. Kryst. Min.*, 1915, **54**, 545—569; 1916, **55**, 321—352).—I. A theoretical paper, in which the author discusses the mathematical theory of crystal structure, with particular reference to the work of W. H. and W. L. Bragg. The relation between the space lattice and the homogeneous point system is carefully considered, and special emphasis is laid on the importance of the notion of the "Fundamentalbereich," or the space appropriated by each point in a point system. This conception is of considerable chemical importance. In a simple point system, each fundamental space contains generally one point, and every point is chemically and structurally similar. In a chemical compound, however, which is represented by a number of similar interpenetrating point systems, each fundamental space must contain one point of each point system, or, in other words, one of each kind of atom in the molecule. The atomic complex situated in the "Fundamentalbereich" corresponds, therefore, with a molecule.

Just as the "Fundamentalbereich" is subject to the coincidence movements appropriate to the symmetry of the system, that is, translations, rotations about an axis, and reflections in a plane, so the atomic complex is subject to these movements. It follows that the atomic complexes are not of necessity all similarly orientated in the structure, and may be present in enantiomorphous forms. If the structure contains complexes of only the one kind or the other, a right- or left-handed crystal results. It is to be noted that the symmetry or structure of the atomic complex situated in the fundamental space does not affect the symmetry of the structure as a whole. The latter is determined by the elements of symmetry which bring about the homogeneous repetition in space of the atomic complex. The complete system of atomic complexes produced by subjecting one of them to all the coincidence movements appropriate to the symmetry of the structure constitutes a group, which is contained in the fundamental space lattice.

It is shown that in certain cases the assumption of symmetrical atoms or points leads to higher symmetry than if the atoms be supposed asymmetric.

In a discussion on the structure of diamond, it is shown that the structure found by Bragg can be deduced by means of the general mathematical theory from a knowledge of the number of carbon atoms, 8, in the elementary cube. The same is true of zinc blende and potassium chloride.

II. Contains a further discussion of the properties of homogeneous point systems. The relation between such point systems and atomic complexes in a crystal structure is very fully discussed, and, in the light of the work of W. H. and W. L. Bragg, the structures of pyrites and quartz are deduced by means of the general mathematical theory of crystal structure. E. H. R.

Resistance Limits of Mixed Crystals and the Molecular Arrangement in Space Lattices. G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1916, 199—265; from *Chem. Zentr.*, 1917, i, 1056—1059).—If a reagent which only attacks the components of a mixed crystal is allowed to act on a series of binary mixed crystals, its action does not increase regularly with the content of the attackable components, but certain limits of resistance are observed. Up to a certain concentration, g_1, of attackable constituents, the mixed crystals, apart from the very small number of attackable molecules, are resistant at the surface to the reagent. If the content of attackable constituent is increased to g_2, this protective action entirely ceases and the reagent can completely dissolve or attack the susceptible component. With regard to their behaviour towards a reagent which only attacks one constituent, the series of mixed crystals can be divided into three portions: (1) the series containing from 100 to g_2 % of attackable constituent from which the latter can be completely withdrawn. (2) The series having from g_2 to g_1 % of attackable constituent, from which the reagent can only remove a portion of the latter. In the residues, the amount of attackable constituent diminishes with its increasing content in the original crystals. (3) The series having from g_1 to 0% of attackable constituent. In this case only so much of the latter is lost as is contained in the molecules on the surface of the crystal, which is therefore practically resistant to the reagent.

Three methods of determining the resistance limits are described; the first depends on a series of quantitative estimations, and requires considerable quantities of material, whilst the second avoids analytical determinations and can be performed on minute quantities of substance. In the third method, the *E.M.F.* of the alloy in solutions of its less noble constituent is determined against some other electrode. Mixed crystals from g_1 to pure noble metal show the potential of the latter; from the point g_1 the potential falls rapidly. The resistance limits of Cu–Au and Ag–Au mixed crystals have been thoroughly investigated for a variety of reagents, and the results are shown in a series of tables, for which the original must be consulted.

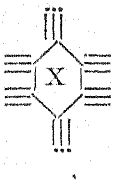
Ag–Au general, the resistance limits of Cu–Au are similar to those of
metals ain mixed crystals. The action of chlorides of the platinum
the affinity d of gold chloride is, however, exceptional. In this case
solutions contaf silver for chlorine is evidenced, and, in consequence,
differently towardning chlorides with eliminable chlorine atoms behave
ism of the reactionls Ag–Au and Cu–Au alloys. When the mechan-
the action of a reagenis similar, there appears to be no difference in
in the mixed crystals ant towards the two series. If the silver atoms
atoms. The action of oxe univalent, the same is true of the copper
the Cu–Au alloy shows diffygen from different oxidising agents on
oxidising agents are active afferent resistance limits. The strongest
powerful (acid solution of V_2, the limit $g_1=4/8$ mol. Cu, the less
weaker at $g_1=6/8$ mol. Cu. Tl_2O_5) at $g_1=5/8$ mol. Cu, and the
is analogous. The mercury ion she action of sulphur and selenium
hows an abnormal behaviour by

diffusing into the alloy without replacing an equivalent amount of copper. With solutions of silver salts and osmium chloride, strongly marked resistance limits occur at $g_1 = 7/8$ mol. Cu. Distinct resistance limits are not observed with mixed crystals of antimony and bismuth, but the rate of reaction decreases discontinuously with variation in the composition of the alloy.

The resistance limits of regular mixed crystals of gold lie at molecular fractions which are multiples of 1/8, and, with the hexagonal Sb–Bi mixed crystals the rate of action of different reagents alters abruptly at multiples of 1/6. A regularity exists here which, like of Law of Multiple Proportions, demands an atomistic explanation. In order to connect the resistance limits with the atomic structure, the disposition of the two kinds of molecules in the lattices must be known. If this is established, special properties of the reagent and of the active molecules of the mixed crystals can be deduced from the resistance limits. According to the properties of the crystals, an 8-point or 14-point lattice is involved. The resistance limits can be deduced from the molecular disposition which corresponds with the most thorough admixture of the two types of molecule which is compatible with the lattice symmetry.

H. W.

Topic Parameters in the Light of the Stereo-Hexite-Pentite Theory. W. Asch and D. Asch (*Zeitsch. Kryst. Min.*, 1915, **54**, 587—589).—The crystal structure of dihydrogen-potassium and dihydrogen-ammonium phosphates and arsenates were examined by Muthmann, who came to the conclusion, from a study of their topic parameters, that whereas replacement of potassium by ammonium or vice versâ produced an appreciable change in the dimensions of the structure in one direction only, the replacement of phosphorus by arsenic or vice versâ resulted in a general expansion or contraction in the structure in all directions.



The present authors formulate these salts as $3R_2O,6H_2O,3X_2O_5$, in accordance with the hexite-pentite theory, and propose the adjoined structural formula, in which the hexagon represents $3P_2O_5$ (or As_2O_5), the lines without dots represent OH-groups and those with dots OK-groups. The authors claim that the effect of isomorphous substitution of K for NH_4 or of P for As on a structure of this type will be in agreement with Muthmann's conclusions, which therefore lend support to the theory.

E. H. R.

The Influence of Temperature Variations on the Formation of Crystals. A. Schubnikov (*Zeitsch. Kryst. Min.*, 1914, **54**, 261—266).—Crystals left for some time in a saturated solution gradually lose their shape and tend to form a layer or disk on the bottom of the vessel. This phenomenon is attributed to alternate rise and fall of temperature. If the temperature rises, the crystal dissolves more at the top than at the bottom, whilst the solution tends to become more concentrated at the bottom, under the influence of gravity. Consequently, on cooling again, crystals are deposited more at the bottom.

The phenomenon of the growth of some faces of a crystal at the expense of others might be explained, if the process were an isothermal one, by the faces having different solubilities at one and the same temperature, so that at a particular temperature the solution might be under-saturated with respect to one face and supersaturated with respect to another. A more probable explanation, however, attributes the phenomenon to temperature variations. Experiments with potassium alum confirm this idea. For these experiments a special apparatus was designed, electrically controlled, by means of which a slow periodic variation of temperature was obtained. In the cube face of a crystal of alum a depression was made and was filled with saturated alum solution, the crystal being then placed in the apparatus for two days. At the end of this time the faces {100}, {110}, {111}, and {112} had appeared in the depression. Other experiments of a similar kind produced similar results.

The formation of concentric layers in the case of alum crystals is attributed to temperature variation and the enclosure of mother liquor. E. H. R.

The Relation between Rate of Growth and External Symmetry of Crystals. A. Schubnikov (*Zeitsch. Kryst. Min.*, 1914, **54**, 267—272).—In a previous paper (A., 1913, ii, 1031) it was shown that crystals deposited from a highly supersaturated solution are more symmetrical externally than those deposited from a less supersaturated solution. In the present paper, experiments with sodium chlorate are described, in which a crop of crystals is caused to be deposited from solutions of varying degrees of supersaturation. From seventy to eighty crystals of each crop were examined by determining the ratio of the lengths of the horizontal cube edges. The mean deviation of this ratio from unity was then determined by the method of least squares and compared with the degree of supersaturation. The results show clearly that the external symmetry of the crystals increases with the degree of supersaturation of the solution. E. H. R.

X-Ray Analysis of the Crystal Structure of Rutile and Cassiterite. C. M. Williams (*Proc. Roy. Soc.*, 1917, A, **93**, 418—427).—Well-formed crystals of the two isomorphous minerals were examined by means of the *X*-ray spectrometer, a special device being adopted in order to compensate for variations in the intensity of the source of the rays. The model of the crystal structure deduced from the experimental data differs essentially from that devised by Vegard for the same group of minerals, including zircon, the present author disagreeing with some of Vegard's experimental observations (A., 1916, ii, 405). The model now put forward possesses holohedral tetragonal symmetry, having a tetragonal screw axis and showing both {100} and {111} planes as cleavage planes. The enantiomorphous character of the structure may be correlated with the peculiar twinning of rutile and cassiterite.

The spectra obtained from corresponding faces of the two minerals are remarkably similar, although it might have been expected that in the case of rutile the greater relative mass of the oxygen atoms might modify the intensities of some of the orders of spectra. E. H. R.

The Purification of Salts by Clarification or by Fractional Crystallisation. E. Rengade (*Compt. rend.*, 1917, **165**, 237—240).—When a mixture of two soluble salts having no common ion, such as ammonium nitrate and sodium chloride, is treated with a small quantity of water at the ordinary temperature, the sodium chloride disappears and is replaced by sodium nitrate and ammonium chloride. If the amount of water is increased progressively, the three salts, ammonium nitrate, sodium nitrate, and ammonium chloride dissolve simultaneously, the second in greater proportion than the third. The composition of the liquid remains constant until the whole of the sodium nitrate is dissolved. When this solution is removed and more water added, then the two ammonium salts dissolve in proportion to their simultaneous solubilities until the whole of the ammonium chloride is removed and the ammonium nitrate remains pure. Thus the purification requires two stages, and it is only necessary to determine by analysis the composition of the two corresponding saturated solutions to calculate the minimum amount of water necessary for the complete purification of one salt in a given mixture at a given temperature. W. G.

Orientation of Anisotropic Liquids on Crystals. F. Grandjean (*Bull. Soc. franç. Min.*, 1916, **39**, 164—213; from *Chem. Zentr.*, 1917, ii, 40).—According to Mauguin (*Compt. rend.*, 1913, **156**, 1246), the drop of an anisotropic liquid is orientated in a definite manner when placed on a crystal face or cleavage fissure of muscovite. The author has independently been led to the following conclusions. Orientation of anisotropic liquids is caused by contact with crystals when it occurs at a surface of perfect cleavage, and the nature of such orientation is generally very simply related to the symmetry of the crystal. Observations were made with orpiment, blende, phlogopite, brucite, talc, pyrophyllite, rock salt, sylvine, and leadhillite, the anisotropic liquids employed consisting of azoxyphenetole, azoxyanisole, anisaldazine, ethyl azoxybenzoate, and ethyl azoxycinnamate. The differences observed during the use of the different crystals and liquids, as well as the methods of investigation, are described in the original. H. W.

The Theory of Gels as Systems of Two Liquid Phases. Emil Hatschek (*Trans. Faraday Soc.*, 1916, **12**, 17—20).—On the assumption that gels consist of two liquid phases, one of which forms polyhedra and the other thin separating films, the apparent elasticity on deformation must be due to the surface energy, any deformation increasing the internal surface. Calculations for the cube, rhombohedron, rhombic dodecahedron, and Kelvin's tetrakaidecahedron show that, the volume of the gel remaining constant, the stress increases until the structure has been extended to 2·52 times its original length, and then slowly decreases. Actual experimental curves, so far as they have been determined, fail to correspond in shape with that theoretically deduced. Rubber has been regarded as a gel, and its stress–elongation curve departs still more widely from the theoretical form. The two-liquid structure of gels is therefore improbable. C. H. D.

Determinations of the Compressibility of Disperse Systems. ARNE WESTGREN (*Zeitsch. anorg. Chem.*, 1916, **95**, 39—63).—The indirect method of determining the compressibility of colloids by measuring the number of particles in a geometrically limited volume at intervals of time (Svedberg and Inouye, A., 1911, ii, 703) is inaccurate, owing to the difficulty of delimiting the volume under observation, variations in the illumination and lack of uniformity in the colloidal particles being contributory causes of error. With high concentrations and fine hydrosols, the difficulty of counting the particles is also considerable. By diminishing the illumination and increasing the dimensions of the illuminating beam, more constant results are obtained. Observations of gold hydrosols of great uniformity (Zsigmondy, this vol., ii, 364) show that when the concentration is not greater than seventy-two particles per 1000 μ^3, the laws of Boyle and of Gay-Lussac hold good exactly. C. H. D.

Colour Change and Degree of Dispersity of Indicators. H. R. KRUYT and J. M. KOLTHOFF (*Kolloid Zeitsch.*, 1917, **21**, 22—26).—In view of the statement (Ostwald, A., 1912, ii, 439) that the colour changes of indicators are frequently accompanied by and may be attributed to changes in the degree of dispersity of the indicators, experiments have been made with a number of indicators, in which the colour of the solution, the Tyndall effect, and the ultramicroscopic appearance were examined in acid, neutral, and alkaline solutions. The results obtained show that there is no evidence to support the view that the degree of dispersity of the indicator is the determining factor in connexion with the colour change. H. M. D.

The Rhythmic Precipitation of Colloidal Mercury. HAROLD S. DAVIS (*J. Amer. Chem. Soc.*, 1917, **39**, 1312—1314).—A method is described by which the author has obtained rhythmic precipitation of metallic mercury by the interaction of an aqueous solution of mercurous nitrate and an agar-agar jelly containing sodium formate. The agar-agar solution is drawn up into narrow glass tubes, where it sets to a jelly, and the tubes are then placed horizontally at the bottom of a dish containing a 2% solution of mercurous nitrate, slightly acidified, the dish being kept at a temperature of about 50° for twelve hours. It is suggested that the formation of the banded deposit is due to the production of supersaturated solutions of colloidal mercury, and is cited as evidence in favour of the existence of supersaturation in colloidal solutions. H. M. D.

Formation of Layers in Suspensions of Soils and Clays. Their Explanation and their Application in the Investigation of Soils for Agricultural Purposes. PAUL EHRENBERG, ERNA HAHN, and OTTO NOLTE (*Kolloid Zeitsch.*, 1917, **21**, 1—19).—The literature relating to the formation of layers in suspensions is reviewed, and an account is given of new experiments which have been made with suspensions of ultramarine. Measurements of the concentration of the suspended substance and of the number of the particles in the more or less sharply differentiated layers indicate that the stratification is due to the circumstance that the size of the particles varies in such a way that the particles fall into discontinuous groups. In each of these groups the particles approximate in size to the mean value which is characteristic of the group; this is, moreover, appreciably different from the mean size of the particles belonging to the neighbouring groups. H. M. D.

Similarity of the Action of Salts on the Swelling of Animal Membranes and of Powdered Colloids. JACQUES LOEB (*J. Biol. Chem.*, 1917, **31**, 343—362).—Dried pig's bladder, freed from fat, when treated for a short time with a *M*/8-sodium chloride solution, swells considerably more when subsequently put into distilled water than it does if it remains permanently in the same salt solution or when it remains permanently in water without a previous salt treatment. The increased swelling appears to be due to an interaction between the salt and a constituent (probably protein) of the membrane, the resulting compound being capable of taking up more water than the untreated membrane. The subsequent swelling in water is apparently inhibited by an excess of salt, because the membrane remaining in salt solution does not swell so much as the membrane treated first with salt and then placed in water or very dilute salt solution. Salts with bivalent cations do not cause the increased swelling observed with sodium chloride; further, the addition of about 8 c.c. of *M*/8-calcium chloride solution to 100 c.c. of *M*/8-sodium chloride solution prevents the after-effect which a treatment with a pure *M*/8-sodium chloride solution produces. Similar effects are observed when the animal membrane is replaced by powdered gelatin or ovomucoid (and probably other powdered colloids), but not by solid blocks or sheets of gelatin, which suggests that the salt effects are due to an action on the surface of colloidal particles (fibres in the case of pig's bladder). This suggestion is supported by the fact that the effect of a previous treatment with the salt solution on the subsequent swelling of a given mass of powdered gelatin in water is greater when the size of the particles is smaller, and hence the total internal surface greater. The mechanism of this swelling is apparently of a different nature from that observed in solid masses of gelatin under the influence of acid or alkali (compare Procter and Wilson, T., 1916, **109**, 307).

Experiments are described showing that the effect of salt on the subsequent rate of percolation of water through a layer of powdered gelatin varies inversely with the rate of swelling. A previous treatment with *M*/8-sodium chloride solution retards the percolation of water through the powdered gelatin, whilst a previous treatment with *M*/8-calcium chloride does not have any such effect. The addition of a small quantity of calcium chloride to the sodium chloride prevents the subsequent retardation of the rate of percolation of water, as it prevents the swelling.

The rate of percolation of water through finely powdered soil previously treated with various salt solutions is affected in the same manner as has been described in the case of powdered gelatin, but swelling of the particles of soil does not seem to take place.

H. W. B.

Ultramicroscopic Investigation of the Tanning Process in Jellies. W. Moeller (*Kolloid Zeitsch.*, 1917, **20**, 257—270).—A further description is given of the conditions of formation of laminated structures in the action of aqueous solutions on jellies. The formation of an insoluble salt by the interaction of an electrolyte in the aqueous solution and a second electrolyte in the jelly is not an essential condition in the production of such structures. It has been found that an aqueous solution of silver nitrate when left in contact with a gelatin jelly containing no added electrolyte, gives rise to the formation of alternating layers. This cannot be attributed to the presence of small quantities of chlorides and phosphates in the jelly, for the same result is obtained when pure gelatin is used. The laminated structure would indeed seem to be produced when any ionisable salt diffuses into a jelly. The same heterogeneous structure results when gelatin jellies are subjected to the action of tanning solutions.

The laminated structures produced under specified conditions are illustrated by photographs and described in detail. It is considered that the ultra-microscope observations cannot be interpreted satisfactorily in terms of the hypotheses which have been previously put forward, and that the rhythmic lamination can only be accounted for in terms of the structure of the jelly. The author's view that gelatin consists of a fibrillated substance (α-gelatin), the spaces between the fibrils being filled by a structureless substance (β-gelatin), is made the basis of an explanation of the rhythmic effects which are the result of the diffusion processes which occur when jellies are brought into contact with solutions of salts. For details the original must be consulted. H. M. D.

In-, Uni-, and Bi-variant Equilibria. XVI. & XVII. F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 1196—1205, 1205—1217. Compare this vol., ii, 299, 411).—A further theoretical discussion of types of equilibrium, with special reference to equilibria of n components in n phases at constant pressure. H. M. D.

Determination of the Heterogeneous Equilibrium of Water Vapour, particularly in the case of Iron and Tungsten. LOTHAR WÖHLER and W. PRAGER (*Zeitsch. Elektrochem.*, 1917, **23**, 199—206).—An apparatus is described, by which, through the use of a Sprengel mercury pump, a gas volume may be made to circulate at any given diminished pressure. This apparatus is used in the determination of the water-vapour equilibria in the case of iron and tungsten. The temperature curves of the reactions are shown to cut at 840°. The equilibrium relationship for tungsten at 940° is $K_{940^\circ}=1·0$. Above 840°, iron is more noble than tungsten. The continuous action of water vapour on tungsten at high temperatures is attributed to the formation of a volatile tungsten oxide. J. F. S.

Heterogeneous Equilibria between Aqueous and Metallic Solutions. The Interaction of Mixed Salt Solutions and Liquid Amalgams. IV. The Ionisation Relations of Sodium and Strontium Chlorides in Mixtures. G. McP. SMITH and S. A. BRALEY (*J. Amer. Chem. Soc.*, 1917, **39**, 1545—1576).—In continuation of previous investigations (compare this vol., ii, 247), experiments have been made with a view to the elucidation of the ionisation relations in solutions containing sodium chloride and strontium chloride. The method of procedure has been previously described, and the data obtained afford directly information relative to the equilibrium between a liquid amalgam containing sodium and strontium and solutions of the chlorides of sodium and strontium. The mass-law constant,

$$C_c=[\mathrm{SrHg}_m][\mathrm{NaCl}]_c^2/[\mathrm{NaHg}_m]^2[\mathrm{SrCl}_2]_c,$$

in which $[NaHg_m]$ and $[SrHg_m]$ are the atomic fractions of the amalgamated metals and [NaCl] and $[SrCl_2]$ the mol. fractions in the salt solution does not actually remain constant when the concentrations of the amalgam and of the salt solution are varied. It increases with the concentration of the amalgam, and for solutions which contain equivalent quantities of the two salts it decreases rapidly until the concentration reaches $0·8N$, then more slowly, and attains a nearly constant value at $1·6N$. The observed relations indicate that the sodium ion fraction increases with increasing salt concentration up to $1·6N$, whilst there is a corresponding decrease in the strontium ion fraction. The value of C_c also depends on the temperature, and increases appreciably when the temperature is raised from 15° to 30°. H. M. D.

Tri-iodide and Tri-bromide Equilibria, especially in Cadmium Solutions. R. G. VAN NAME and W. G. BROWN (*Amer. J. Sci.*, 1917, [iv], **44**, 105—123).—The influence of the metal on the equilibrium in solutions containing free halogen and metallic haloids has been investigated by the distribution method. The results obtained with strontium, nickel, zinc, and lanthanum iodides show that the equilibrium constant, $k=[\Sigma I][I_2]/[\Sigma I_3]$, has the same value as for the iodides of the alkali metals. On the other hand, for solutions of cadmium iodide the value of k is much larger and increases rapidly with increasing iodide concentration. Similar abnormality is shown by solutions which contain potassium iodide, together with cadmium or mercuric iodide. The corresponding constant for the bromine–bromide equilibrium shows abnormality of the same type in the case of cadmium bromide solutions and of solutions which contain potassium bromide together with cadmium or mercuric bromide. The abnormality is attributed to the presence of complex molecules or ions, and on the assumption that these do not combine with the halogen, it is shown that the measurement of the equilibrium constant k affords a method for the determination of the proportion of complex molecules and ions. From the results obtained with solutions which differ in respect of the iodine or bromine content, it is possible by extrapolation to determine the extent to which complex molecules are present in pure solutions of the metallic haloids. In this way it has been found, for instance, that 0·5, 0·25, 0·125, and 0·01 molar solutions of cadmium iodide contain respectively 6·0, 10·6, 16·8, and 55·0% of active iodide.

H. M. D.

The Effect of Pressure on the Equilibrium Constant of a Reaction in a Dilute Solution. A Simple Proof of the Expression. W. C. McC. Lewis (*Trans. Faraday Soc.*, 1917, **12**, 314—316).—The general expression $d \log K/dP =$ volume shrinkage$/RT$ has been obtained by Planck and others by means of the thermodynamic potential. A simpler deduction may be arrived at from the principle of maximum work.

C. H. D.

Equilibrium in Silicate Fusions and the Determination of the Melting Point of Calcium Silicate. C. Doelter (*Sitzungsber. k. Akad. Wiss. Wien, math-nat. Klasse*, 1911, **110**, 839—864; from *Zeitsch. Kryst. Min.*, 1914, **54**, 398).—The melting points of many silicates, determined by the thermal method, are too high owing to under-cooling or over-heating. With few exceptions (sodium, lithium, and lead silicates), there is no distinct melting point, the substance passing gradually from the crystalline, through a glassy, amorphous stage to the liquid condition over a certain temperature interval.

The thermal method being applicable only to quickly melting substances, the author employs (1) an optical method, using a hot microscope, whereby the melting process is observed directly, or (2) an approximate method, the finely powdered silicate being kept at the sintering temperature until the mass melts completely.

The influence of the size of the particles may amount to 100° or more. The rate of heating is important, and the velocity of melting or crystallising depends also on viscosity. It follows that the laws deduced from the phase rule and from thermodynamic principles apply to silicate fusions only in a modified form.

As a result of the non-observance of the above principles, large errors may arise. Whilst Day and Genossen found for wollastonite a melting point of 1260° and for calcium α-metasilicate 1512°, the author finds 1240—1320° and 1310—1380° respectively. A molecular change of wollastonite into the α-form was not observed, but it was noticed that above 1260° only the α-silicate separated. E. H. R.

Uniform Pressure, Deformation Pressure, and Rock Metamorphosis. PAUL NIGGLI (*Zeitsch. anorg. Chem.*, 1916, **95**, 64—78. Compare A., 1915, ii, 242; Hasselblatt, A., 1916, ii, 299; Wegscheider, *ibid.*, 299).—The minerals in a primary (igneous or sedimentary) rock may either be in a state of true equilibrium or in one of almost complete inertia, owing to the low velocity of transformation. The number of components being usually at least nine, chemical changes almost always take place in the system when the external conditions are altered, plasticity and gliding playing, in the case of silicate rocks, no important part. The recrystallisations which take place in geological time are usually due to solution and re-deposition, especially with capillary water as the solvent. Non-uniform stress accelerates the change by, for example, increasing the solubility. The newly formed minerals are usually not those which result from magmatic fusion, but those which are formed by hydrothermal methods below 450°. This is illustrated by photomicrographs of chloritoid schists, the large porphyroblasts of chloritoid being surrounded by clear spaces, filled with quartz and chlorite. Actual flow of a solid phase into the capillary spaces probably does not take place in silicate rocks. It is not possible to apply definite formulæ on account of the indefiniteness of the stresses and of the fact that equilibrium is not attained.

C. H. D.

Does the Law of Mass Action Regulate Diastatic Reactions? OCTAVE BAILLY (*Compt. rend.*, 1917, **165**, 248—250; *J. Pharm. Chim.*, 1917, [vii], **16**, 161—167).—Taking the results given by Bourquelot and Verdon (compare A., 1913, i, 542, 781) for the synthesis of β-methyl glucoside, the author has calculated the quantity of dextrose converted into glucoside from the equation $K=x(c+x)/(a-x)(b-x)$, where a, b, and c represent the molecules of methyl alcohol, dextrose, and water present at the commencement of the reaction, and x the molecules of dextrose converted. The first five values of x calculated agree exactly with the experimental values, and the last five show a difference of 2%. These results are considered to support an affirmative answer to the question. W. G.

Hydrolysis of Acetanilide. DAVID R. MERRILL and ELLIOT Q. ADAMS (*J. Amer. Chem. Soc.*, 1917, **39**, 1588—1598).—The hydrolysis of acetanilide in presence of hydrochloric acid proceeds at a rate which is proportional to the product of the concentrations of the unhydrolysed acetanilide and the hydrogen ion. The value of the velocity coefficient at 100° is 8·4 when the hour is taken as the unit of time. The equilibrium constant for the reaction $NHPh\cdot COMe + H^{\cdot} + H_2O \rightleftharpoons NH_3^{\cdot}Ph + MeCO_2H$ is found by extrapolation to be $K = 950$, from which the velocity coefficient for acetylation is found to be 0·0089 (time in hours). H. M. D.

Catalysis. Part III. Some Induced Reactions. Nilratan Dhar (T., 1917, **111**, 690—706. Compare A., 1916, ii, 236).—Under ordinary conditions, and even on boiling, oxalic acid and other reducing agents do not reduce mercuric chloride to mercurous chloride. The author has investigated the action of various inductors on this and several similar reactions. The action of the oxidising agents, potassium persulphate, manganese dioxide, potassium nitrite, potassium permanganate, chromic acid, and nitric acid, on the reduction of mercuric chloride by oxalic acid has been studied. From the results, it is shown that the greater the concentration of the inductor, the greater is the amount of mercurous chloride obtained; this relation holds up to a certain limiting concentration of the inductor, after which an increase in the concentration of the inductor is accompanied in most cases by a decrease in the amount of mercurous chloride. The higher the temperature, the greater the amount of mercurous chloride formed. The greater the concentration of the actor, the greater the amount of reduction. Sulphuric acid hinders and manganese sulphate promotes the reaction. A similar series of experiments with some of the inductors has been carried out with tartaric acid, malic acid, malonic acid, glycollic acid, citric acid, hydrazine hydrochloride, and hydroxylamine hydrochloride, in each case with mercuric chloride. Similar results were obtained in all cases. A number of other reactions have been studied, including the reduction of copper chloride by organic acids in the presence of potassium permanganate as inductor; gold chloride by organic acids with various inductors; silver nitrate and organic acids in the presence of potassium permanganate as inductor, and sodium selenite and various reducing agents in the presence of potassium permanganate as inductor. A number of conductivity determinations have been carried out of some induced reactions. Experiments were made with oxalic acid and malonic acid as actors, mercuric and gold chlorides as acceptors, and potassium permanganate as inductor. The conductivity of the reaction mixture falls off very rapidly at first, and as soon as the reduction of the metallic salt begins, the conductivity again rises slowly. The results are discussed and tentative theories put forward to explain the results. J. F. S.

Catalysis. IV. Temperature-coefficients of Catalysed Reactions. Nilratan Dhar (T., 1917, **111**, 707—762. See preceding abstract).—The author has studied the kinetics of the reduction of mercuric chloride by oxalic acid in the presence of catalysts, the oxidation of oxalic and formic acids by chromic acid, and the oxidation of oxalates and formates by iodine, mercuric chloride, and silver nitrate. In the case of the oxidation of oxalic acid by chromic acid, it is shown that the reaction is unimolecular with regard to chromic acid and termolecular with regard to oxalic acid at 25°. The whole reaction is therefore quadrimolecular and may be represented by $H_2Cr_2O_7 + 3C_2H_2O_4 = Cr_2O_3 + 4H_2O + 6CO_2$, the neutralisation of the chromic oxide by oxalic acid being extremely rapid, and consequently not affecting the velocity of the reaction. It is shown that with increasing concentration of chromic acid, the velocity constant decreases, and this is attributed to the reaction between the oxalic acid and chromic oxide taking place with different velocities with changing concentration of oxalic acid. The temperature-coefficient of the velocity constant varies with temperature, the following values being found: between 25° and 30°, 1·95; between 50° and 60°, 1·72. In the presence of sulphuric acid of moderate concentrations, the velocity of the oxidation is increased, but a large excess of sulphuric acid retards the reaction. The temperature-coefficient is unaltered by the presence of sulphuric acid in moderate concentration, but in the presence of a large excess of sulphuric acid it is increased. In the presence of manganese sulphate as catalyst, the reaction is independent of the concentration of the chromic acid. The effects of molybdic acid, ammonium molybdate, and boric acid as catalysts of the oxidation of oxalic acid by chromic acid have also been studied. In the case of the oxidation of formic acid by chromic acid, the reaction is unimolecular with respect to chromic acid and termolecular with respect to formic acid, and may be represented $H_2Cr_2O_7 + 3H{\cdot}CO_2H = Cr_2O_3 + 6H_2O + 3CO_2$. No disturbing factors are observed in this case with change of concentration. The temperature-coefficient is 2·05, and is not influenced by change in concentration. The velocity of oxidation is much increased in the presence of sulphuric acid, and the temperature-coefficient is much reduced. Manganese sulphate retards this reaction, but has no influence on the temperature-coefficient. The influence of molybdic acid and manganese chloride as catalysts of this reaction has also been studied.

The oxidation of sodium formate by iodine is shown to be unimolecular with respect to both iodine and sodium formate; the whole reaction is therefore bimolecular, and may be represented $H{\cdot}CO_2Na + I_2 = HI + NaI + CO_2$. The reaction is retarded by iodine ions and has a temperature-coefficient of about 4, which is not changed by the negative catalyst, potassium iodide. Manganese sulphate retards the reaction, the velocity constant decreasing with increasing concentration of manganese sulphate.

The oxidation of sodium formate by mercuric chloride is unimolecular with regard to both substances, and consequently is a bimolecular reaction. The equation employed to represent the change would demand a termolecular reaction, which indicates that this reaction must occur in stages. This reaction has a temperature-coefficient of 3·63 and is retarded by manganese sulphate. This reaction is retarded by sodium acetate and the chlorides of sodium, zinc, calcium, manganese, and strontium. In each case the temperature-coefficient is increased.

Silver nitrate is reduced by sodium formate according to a bimolecular reaction, of which the temperature-coefficient is 2·67 between 25° and 40° and 2·48 between 40° and 50°. Manganese sulphate acts as a negative catalyst in this reaction without changing the temperature-coefficient.

A number of experiments have been carried out both in the dark and in light with the object of ascertaining the mechanism of chemical change and temperature-coefficient. In the case of the oxidation of quinine sulphate by chromic acid, it is shown that in the dark the temperature-coefficient is 1·87, whereas in light the lower value 1·04 is obtained. The oxidation of potassium oxalate by iodine is shown to be unimolecular with regard to both substances; this reaction in the dark has a temperature-coefficient of 7·2 between 25° and 40°, 6·1 between 40° and 50°, and 5·4 between 50° and 60°; in diffused daylight, the reaction velocity is found to be less than in the dark and to have a temperature-coefficient of 3·36 between 25° and 50°. The oxidation of potassium oxalate by mercuric chloride in the dark at 99·6° is bimolecular, although it would appear from the equation to be termolecular The temperature-coefficient is 2·2 in the dark and 1·19 in the light. J. F. S.

A New Case of Reversible Catalysis: Direct Formation of Nitriles from Amines with the same Carbon Chain.

Paul Sabatier and G. Gaudion (*Compt. rend.*, 1917, **165**, 224—227).—In certain cases, the authors have been able to obtain the reverse of the catalytic hydrogenation of nitriles to amines by means of finely divided nickel (compare Sabatier and Senderens, A., 1905, i, 267). Thus, if the vapour of benzylamine is passed over nickel at 300—350°, benzonitrile is obtained. At the same time, the hydrogen produced in this process reduces more of the amine, giving toluene and ammonia, the whole course of the reaction being $3C_6H_5{\cdot}CH_2{\cdot}NH_2 = C_6H_5{\cdot}CN + 2C_6H_5{\cdot}CH_3 + 2NH_3$. Similarly, *iso*amylamine yields *iso*valeronitrile, *iso*pentane, and ammonia, the reaction being further complicated in this case, since a portion of the *iso*pentane is decomposed by the nickel, carbon being deposited. With methylamine, good results are not obtained, probably owing to the action of the hydrogen cyanide on the nickel. Copper is not such a good catalyst as nickel for this reaction. W. G.

Elements neither Free nor Combined. A Third State.

Carl Hering (*J. Amer. Chem. Soc.*, 1917, **39**, 1619—1623).—A plea for the recognition of ions as representing a third state in which the elements are neither free nor combined. H. M. D.

Numerical Relationships between Atomic Weights.

Rudolf Vondráček (*Chemické listy*, 1917, **11**, 33—37; from *Chem. Zentr.*, 1917, i, 840).—The theory that certain, if not the majority, of chemical elements are mixtures of several isotopic elements of different atomic weight has not been supported by the results of previous investigations. The approximately integral atomic weights of the elements of the series H–Co has been regarded as a consequence of genetic relationships; the author now shows that the heavy elements are related to one another as well as to those of the two short periods by definite and regular differences in the atomic weights. If the atomic weights of the elements of the two short periods the ordinal numbers of which are multiples of 3 (Li, C, F, Mg, P, Ar) are increased by 95·9, the atomic weights of the elements of the series Rh–I with uneven ordinal numbers (Rh, Ag, In, Sb, I) are derived. When the atomic weights of the same elements, with the exception of lithium and carbon, are increased by 87·7 or 88·1, the atomic weights of the elements of the series Rh–I with even ordinal numbers (Pd, Cd, Sn, Te) are obtained. A similar relationship connects the elements of uneven ordinal numbers (Ag, In, Sb, I) with those of the ordinal numbers 10, 13, 16, 19. Not only the atomic weight, but also the position of the derived element in the natural system, is accurately and definitely determined by these relationships; tellurium and iodine fall naturally into the places assigned to them on the basis of determinations of atomic weight. Similar relationships are found in other portions of the system. H. W.

Valency Centres. O. Hinsberg (*J. pr. Chem.*, 1917, [ii], **95**, 121—131).—A theoretical paper in which the author slightly modifies his earlier views (this vol., ii, 173; A., 1916, i, 725) by assuming the postulated valency centres to be identical with the positively charged atomic nuclei of the electronic theory. The atoms of the elements of groups I to IV of the periodic classification are believed to possess only one valency centre and exhibit a maximum valency of 4, although this is only occasionally exhibited before the carbon group; atoms of the elements of groups V and VI possess two valency centres or atomic nuclei, whilst atoms of group VII may possess two or three. In illustration of the theory, the nitrogen atom is cited as having two nuclei, one of which holds four valency electrons, whilst the other retains only one, and under certain conditions is capable of functioning in a similar manner to the nucleus of the univalent atom of an alkali metal, with the formation of an ammonium salt. The sulphur atom in the sulphonium compounds includes a tervalent and a univalent valency centre, to which the organic groups and the acid radicle are respectively attached. D. F. T.

The Period of the Alchemists Isaac of Holland and Jan Isaac of Holland. H. J. Holgen (*Chem. Zeit.*, 1917, **41**, 643—644. Compare this vol., ii, 198).—Evidence is adduced in support of the view that these alchemists lived in the second half of the sixteenth century. H. M. D.

Filtration with the Exclusion of Moisture and Air. G. Reddelien (*Chem. Zeit.*, 1917, **41**, 580).—A glass bell, provided with a side-tube and a tubulure at the top, is fitted over an ordinary

Büchner funnel. The side-tube is connected with absorption vessels, so that air free from moisture or carbon dioxide may be admitted into the funnel. The liquid to be filtered is introduced into the funnel through a funnel fixed in the tubulure; the stem of this second funnel is closed by a rod which is ground to fit into the stem. The join between the rim of the bell and the upper edge of the Büchner funnel is made air-tight by means of a rubber band.

W. P. S.

An Arrangement for the Automatic Washing of Precipitates Filtered with Difficulty. G. Wegelin (*Kolloid Zeitsch.*, 1917, **20**, 270—274).—The apparatus described is a simple arrangement in which the wash liquid is supplied to the filter funnel intermittently, this being effected automatically by a syphon of the type familiar in a Soxhlet apparatus. A further feature of the apparatus is that the filtration is carried out under an excess pressure.

H. M. D.

The Use of Large Glass-stoppered Containers in Autoclaving. Robert B. Krauss (*J. Amer. Chem. Soc.*, 1917, **39**, 1512—1513).—The material which it is necessary to heat in an autoclave may be placed in a glass bottle, tightly stoppered, and this put in an iron autoclave half filled with water. Under proper conditions, the pressure on the glass is the same inside and outside, and bottles have been used in this way up to pressures of 5000 lb. per square inch.

J. C. W.

Lecture Experiments on the Theory of Explosives. J. Eggert and H. Schimank (*Zeitsch. Elektrochem.*, 1917, **23**, 189—192).—Several lecture experiments are described, which are designed to demonstrate the evolution of gas, the varied explosion velocities, and the difference between the decomposition of a primary and a secondary explosive. A further experiment is described to show the difference between deflagration and explosion.

J. F. S.

Inorganic Chemistry.

Electrolysis of Hydrochloric Acid. Paul Hanck (*Zeitsch. physikal. chem. Unterr.*, 1917, **30**, 33—34; from *Chem. Zentr.*, 1917, i, 991).—In order to avoid the absorption of chlorine during the electrolysis of hydrochloric acid, the decomposition is effected in a small U-tube provided with two side-tubes. The electrodes are held in position by rubber stoppers, and do not dip deeply into the acid. The evolved gases are conducted by rubber tubes to the Hofmann's apparatus, which is charged with concentrated sodium chloride solution.

H. W.

Electrolysis of Hydrochloric Acid in Hofmann's Apparatus. Friedrich C. G. Müller (*Zeitsch. physikal. chem. Unterr.*, 1917, **30**, 34—35; from *Chem. Zentr.*, 1917, i, 991—992).—During the electrolysis of hydrochloric acid in Hofmann's apparatus, the cathode liquid should not contain dissolved chlorine, since this is carried forward by the hydrogen; the observed volume of the latter is consequently too great.

If, during the electrolysis of sodium chloride solution, the sodium hypochlorite attains a considerable concentration around the cathode, it exerts an oxidising action and too little hydrogen is evolved. Platinum electrodes are scarcely attacked by the chlorine, whilst thin carbon rods are completely disintegrated after a short time. H. W.

When is a Candle Extinguished in an Enclosed Volume of Air? Friedrich C. G. Müller (*Zeitsch. physikal. chem. Unterr.*, 1917, **30**, 28—30; from *Chem. Zentr.*, 1917, i, 991).—The air in which a candle has burnt until extinguished contains 4—6% carbon dioxide and 15—13% oxygen; deeply expired air has a similar composition. Alcohol, burning on cotton-wool, leaves, after extinction, a gas mixture containing 6·5% carbon dioxide and 11% oxygen. The residue from glowing wood charcoal contains 8% carbon dioxide and 9% oxygen. Burning sulphur leaves 13·5% oxygen. H. W.

The Absorption of Atmospheric Gases by Water. J. H. Coste (*J. Soc. Chem. Ind.*, 1917, **36**, 846—853).—A summary of the work which has hitherto been done on the solubility of air in various waters, including distilled water, rain water, well water, and sea water. T. S. P.

Proof of the Formation of Water by the Union of an Acid and a Base to Yield a Salt. H. Zeitler (*J. physikal. chem. Unterr.*, 1917, **30**, 35; from *Chem. Zentr.*, 1917, i, 991).—A small dry stick of sodium or potassium hydroxide is placed in a jar of dry hydrogen chloride. After a short time, the glass becomes strongly bedewed and the alkali is covered with crystals of salt. H. W.

The Colour and Oxidising Value of some Ozone Solutions. Franz Fischer and Hans Tropsch (*Ber.*, 1917, **50**, 765—767).—When a current of ozonised oxygen is passed through acetic acid, acetic anhydride, ethyl acetate, chloroform, or carbon tetrachloride at the ordinary temperature, a blue solution is obtained (compare Harries and Koetschau, A., 1909, i, 755; Erdmann, A., 1908, ii, 830), the colour persisting for more than fifteen to twenty hours with acetic acid and carbon tetrachloride, but disappearing more rapidly with the other solvents. Water and formic acid do not form coloured solutions, the latter solvent undergoing oxidation to carbon dioxide.

Comparative experiments with a gaseous stream containing approximately 6% of ozone by volume indicated that carbon tetrachloride dissolves seven times as much ozone as an equal bulk of water, and when saturated contains per litre three times as much ozone as the original ozonised oxygen.

The formation of the blue solution of ozone in carbon tetrachloride forms a simple lecture experiment. D. F. T.

Action of Ozone on Inorganic Compounds. C. HARRIES (*Zeitsch. anorg. Chem.*, 1917, **99**, 195—196).—A reply to Riesenfeld and Bencker (this vol., ii, 201). The author's experimental results are not to be explained by the high concentration of the potassium iodide solution, a 2·5% solution only having been used. The action of crude and washed ozone on butylene (A., 1912, i, 343, 407) is evidence of the presence of more than one compound in ordinary ozone. C. H. D.

Black Sulphur. BERNHARD NEUMANN (*Zeitsch. angew. Chem.*, 1917, **30**, i, 165—168).—As a result of the investigation of some black sulphur from Mexico, the author comes to the conclusion that the black sulphur of Magnus and Knapp is not a special modification of sulphur, but ordinary yellow sulphur which has been coloured black by small quantities of carbon or of metallic sulphides (iron and platinum).

The following analyses I, II, and III are of black sulphur from the San Augustin mines, IV of blackish-green sulphur from the San Rafael mines, and V of yellow sulphur from the San Rafael mines:

	S.	C.	$Fe_2O_3(Al_2O_3)$.	CaO.	MgO.	SO_3.	CO_2.	Insol.
I.	58·31	0·53	1·00	11·85	0·52	17·75	—	9·72
II.	58·63	0·59	0·78	12·16	0·82	18·90	—	7·74
III.	60·11	0·77	1·32	11·18	3·77	4·64	10·28	7·64
IV.	91·92	0·13	0·23	2·76	0·14	3·75	—	0·72
V.	99·98	—	—	—	—	—	—	0·02

The presence of carbon in the black sulphur is explicable on the assumption that the hydrocarbons in the volcanic exhalations from which the sulphur is deposited do not come into contact with sufficient air for complete combustion, with the result that carbon is deposited. The microphotographs of black sulphur show the presence of sulphur and amorphous carbon side by side. T. S. P.

Apparatus for the Preparation of Hydrogen Sulphide or Hydrogen. MOSBACHER (*Zeitsch. angew. Chem.*, 1917, **30**, i, 176). —Hydrochloric acid is contained in a bottle situated above the other part of the apparatus, and is allowed to flow in regulated quantity into a bottle containing ferrous sulphide or granulated zinc. This bottle is provided with a delivery tube for the gas evolved, and the gas is passed through a wash-bottle before use. Spent liquor may be drawn off from the lower part of the bottle containing the ferrous sulphide or zinc. W. P. S.

Apparatus for Precipitation with Hydrogen Sulphide under Pressure. AUBREY VAIL FULLER (*J. Ind. Eng. Chem.*, 1917, **9**, 792—793).—The upper opening in an ordinary Kipp generator is closed with a rubber stopper through which pass a small tapped tube and a narrow tube almost a metre long; a bulb is provided at the top of the latter tube. The gas outlet of the apparatus is provided with a two-way tap. The precipitation is carried out in a flask closed with a rubber stopper carrying two tubes, one of which conducts the hydrogen sulphide into the flask, whilst the other carries a length of rubber tubing and a pinch-cock. The latter is closed when the flask is filled with hydrogen sulphide, and, by closing the tap at the top of the apparatus, a pressure column of about a metre may be obtained, the liquid in the generator rising to this height in the long narrow tube. W. P. S.

The Decomposition of Metallic Sulphates by Heat. H. O. HOFMAN and W. WANJUKOW (*Bull. Amer. Inst. Min. Eng.*, 1912, 889—943; from *Zeitsch. Kryst. Min.*, 1915, **55**, 111).—The decomposition of many hydrated and dehydrated metallic sulphates has been studied by heating in an open tube in a current of dry air. The salts examined include ferric and ferrous sulphates, and sulphates of bismuth, aluminium, zinc, lead, copper, manganese, nickel, cobalt, cadmium, magnesium, silver, calcium, and barium. In each case the temperature is recorded at which decomposition begins and that at which it becomes energetic, whilst the gaseous and solid products are described. In general, normal sulphates which form no basic sulphates by decomposition give sulphur trioxide and dioxide as gaseous products, whilst those which form basic sulphates give only sulphur dioxide. By further decomposition of the basic salt into metallic oxide, sulphur trioxide is produced. Metallic sulphates of the bases of the form M_2O_3 or M_2O give no basic sulphates by decomposition. E. H. R.

The Synthesis of Ammonia and the Oxidation of Ammonia to Nitric Acid. EDWARD B. MAXTED (*J. Soc. Chem. Ind.*, 1917, **36**, 777—782).—A general account, without going into details, of the work which has been done by an English Company towards the establishment of a synthetic ammonia industry in Great Britain.

The nitrogen is separated from the air in the first case by passing the air through a separating column, over the plates of which a descending current of liquid nitrogen is allowed to flow. The oxygen is thereby liquefied and the nitrogen passes upwards, whilst the residual mixture of oxygen and nitrogen undergoes fractionation in the lower part of the apparatus; the liquid arriving at the bottom of the column is practically pure oxygen. The hydrogen (99·9% purity) is produced by a modification (not described) of the intermittent method, that is, by the alternate steaming and reduction of iron with water-gas.

The catalysts used to bring about the combination of nitrogen and hydrogen consist of iron containing traces of other substances as promoters. The working pressure is about 180 atmospheres, and the temperature in the catalyst column varies from 600° to 650°.

The oxidation of the ammonia to nitric acid is brought about by iron catalysts containing various promoters, air, or air enriched with oxygen, being used as the oxidising agent. A table is given showing the efficiency at 700° of the following catalysts: iron, iron–thorium, iron–cerium, iron–bismuth, iron–tungsten, iron–copper, iron–lead, iron–antimony, iron–potassium, iron–uranium, iron–calcium, iron–zinc, and iron–manganese. The efficiency of pure iron is very appreciably raised by the addition of cerium, thorium, bismuth, tungsten, or copper, the time of contact for the maximum yield of nitric acid varying with the particular promoter used. The alkali metals appear to have very little effect on the activity of iron, whilst calcium, zinc, and manganese depress very considerably the maximum yield of nitric acid.

Figures are given showing that from the point of view of power and material, the direct synthesis of ammonia is twice as efficient as the cyanamide process and more than six times as efficient as the arc process. T. S. P.

The Antiseptic Properties of Nitrous Air. H. COLIN (*Compt. rend.*, 1917, **165**, 194—196).—The antiseptic power attributed by Priestley (*Phil. Trans.*, 1772, **62**, 210) to nitrous air is really due to the nitric acid formed by contact with the moist air introduced with the animal corpses. W. G.

The Sensitiveness of Azides. LOTHAR WÖHLER and F. MARTIN (*Zeitsch. angew. Chem.*, 1917, **30**, i, 33—39).—The azides investigated were those of silver, lead, mercury (ous), cadmium, zinc, copper (ous), nickel, cobalt, manganese, barium, strontium, calcium, lithium, and thallium. In order to determine the temperature of detonation, varying quantities (0·005, 0·01, and 0·02 gram) of the azides were heated at known temperatures in a special apparatus and the time (in seconds) noted before detonation took place. The azides were used in the form of pastilles. From the curves showing the relation between the weight of azide used and the temperature of detonation, it is found that the temperature falls with increase in weight, the curve ultimately becoming asymptotic towards the axis of weight. The temperature corresponding with the asymptotic portion of the curve is characterised by the authors as the real temperature of detonation; practically, it is the temperature found when 0·02 gram of the azide is used. The detonation temperatures of the various azides, in the order given above, were found to be 297°, 327°, 281°, 291°, 289°, 174°, 200°, 148°, 203°, 152°, 169°, 158°, 245°, and 320° respectively; the thallium azide does not detonate, but only undergoes vigorous decomposition. These temperatures do not show any well-defined regularity, but, generally speaking, the lower the molecular weight of the azide the lower is the detonation temperature. This is quite different from the behaviour of the fulminates, the detonation temperature of which (particulars to be published later) are almost independent of the metallic component. Moreover, the fulminates do not show the same tendency as the azides to give an asymptotic portion of the weight-detonation temperature curve.

The azides of zinc, cobalt, nickel, manganese, calcium, and lithium are hygroscopic.

As a result of the authors' experiments on the azides and fulminates, it is suggested that the detonation temperature for technical purposes should be defined as that temperature below which pressed pastilles of the microcrystalline substances do not detonate even after heating for five minutes; the quantity of substance should be such that it does not all decompose before the detonation temperature is reached. The comparison temperature for the different substances is defined as that at which detonation takes place when 20 mg. of the substance are heated for five seconds.

The sensitiveness of the various azides towards shock, using a falling weight, was also determined, and the curves showing the relation between the quantity of substance and the height of fall of the weight drawn. The curves often show a well defined minimum, so that for the characterisation of the azides the complete curve must be determined. The detonation temperature therefore forms a better criterion for the azides than their sensitiveness towards shock. In the case of thin layers of the azides, the sensitiveness towards shock corresponds with the Dupré friction sensitivity.

The heat of detonation has no noticeable influence on the sensitiveness of the azides. With the fulminates the parallelism between the temperature of detonation and the sensitiveness towards shock is much more marked than with the azides, which only show it between certain limits of weight of substance. T. S. P.

The Structure of Pyrophosphoric Acid. D. Balareff (*Zeitsch. anorg. Chem.*, 1917, **99**, 190—194. Compare A., 1915, ii, 446).—Further evidence is given in favour of an unsymmetrical structure for pyrophosphoric acid. When orthophosphoric acid is dehydrated by boiling with $SOCl_2$, the pyro-acid formed is always accompanied by metaphosphoric acid, whilst when SO_2Cl_2 is used, only the pyro-acid is obtained.

Ethyl metaphosphate, prepared from ethyl ether and phosphoric oxide without heating, combines with ethyl orthophosphate at 185—190°, forming the pyrophosphate. Ethyl metaphosphate does not combine with methyl orthophosphate, but methyl metaphosphate is formed by heating methyl pyrophosphate.

Calcium pyrophosphate reacts with phosphorus pentachloride according to the equation $2Ca_2P_2O_7 + 6PCl_5 = Ca(PO_3)_2 + 8POCl_3 + 3CaCl_2$, and the strontium salt behaves in a similar manner.

C. H. D.

Production of Per-salts (Perphosphates and Perarsenates). S. Aschkenasi (D.R.-P., 296796, 1914; from *J. Soc. Chem. Ind.*, 1917, **36**, 872).—Alkaline earth peroxides can be dissolved in excess of concentrated phosphoric or arsenic acid, forming hydrogen peroxide and the corresponding primary per-salt. The hydrogen peroxide does not decompose, and by evaporation under diminished pressure, with minimum elevation of temperature, the primary perphosphate or perarsenate can be obtained. The corresponding alkali salts can be obtained by decomposing the alkaline earth salts before evaporation with an alkali sulphate. T. S. P.

Production of Anhydrous Per-salts or Mixtures of Per-salts. S. Aschkenasi (D.R.-P. 296888, 1915; from *J. Soc. Chem. Ind.*, 1917, **36**, 872).—Per-salts prepared in a vacuum can be subsequently dried in air at 100° without evolution of oxygen. They soften and again dry, giving off an appreciable quantity of water vapour. Drying in this way improves the stability of the per-salts. T. S. P.

Differentiation of the Internal Structure of Different Species of Silica by their Röntgen Ray Interference Patterns. S. Kyropoulos (*Zeitsch. anorg. Chem.*, 1917, **99**, 197—200).—The method of Debye and Scherrer (*Nachr. K. Ges. Wiss. Göttingen Math.-phys. Klasse*, 1916) has been applied to powdered silica. An amorphous substance in this condition behaves as a grating of low dispersive power, whilst a powdered, crystalline substance behaves as a grating of high dispersive power. The particles used are from 0·5 to 1 μ in diameter, and are lightly pressed into paper tubes and exposed to platinum radiation. Quartz and cristobalite give similar but readily distinguishable systems of rings, whilst interference rings are absent from the patterns of quartz glass and precipitated silica. A silica gel gives a single broad ring. When precipitated silica is heated at 1300° for two hours, interference rings appear, indicating a partial conversion into cristobalite. C. H. D.

The Exchange of Bases in Silicates. I. The Exchange of Alkalis and Ammonia in Hydrated Alumina Alkali Silicates (Permutites). E. Ramann and A. Spengel (*Zeitsch. anorg. Chem.*, 1916, **95**, 115—128).—Sodium permutite is purified by treating with a 10% solution of sodium chloride until calcium is no longer extracted. When small quantities of calcium carbonate are present, more rapid purification is effected by treatment with 10% ammonium nitrate, followed by reconversion of the ammonium permutite into the sodium compound. The granular permutite is freed from small particles, and the reacting solution is run through it at the rate of 50 c.c. per hour. Complete equilibrium is attained in this way.

Sodium permutite yields the same potassium permutite with potassium chloride and potassium sulphate, and the ammonium compound is also completely converted into the potassium compound. The total concentration of the solutions is without influence on the composition of the final product, which is also independent of the nature of the alkali in the original permutite. When mixed solutions of different salts are used, the resulting composition is such as to indicate that the reaction is entirely ionic. It is independent of the nature of the anion. C. H. D.

The Binary Systems of Bromides of the Alkalis and Alkaline Earths. GEORG KELLNER (*Zeitsch. anorg. Chem.*, 1917, **99**, 137—183).—The bromides are melted in Jena glass tubes in an atmosphere of nitrogen, the platinum platinum–rhodium couple being inserted without a protecting sheath. Transparent sections of the solidified mass are made by soaking in Canada balsam and grinding with paraffin. The following melting points of the anhydrous simple bromides are found: LiBr, 552°; NaBr, 742°; KBr, 730°; $MgBr_2$, 711°; $CaBr_2$, 730°; $SrBr_2$, 643°; $BaBr_2$, 847°. All are isomorphous with the corresponding chlorides, with the exception of strontium bromide, which is hexagonal, the chloride being regular. Dimorphism has not been observed. Lithium bromide forms with sodium bromide a continuous series of solid solutions, which probably break up at lower temperatures, as, although thermal or crystallographic changes have not been observed, the crystalline mass expands and disintegrates on cooling. Lithium and potassium bromide form a simple system without solid solutions, the eutectic temperature being 348°. Lithium bromide forms solid solutions of limited concentration with both magnesium and calcium bromides, the liquidus curves being of similar and rather unusual form. With strontium bromide, a double salt, $LiBr,2SrBr_2$, is formed, decomposing at 503°. Lithium and barium bromides have a eutectic point at 483°, and solid solutions are not formed.

Sodium and magnesium bromides form a simple eutectiferous series, the eutectic temperature being 431°. Sodium and calcium bromides solidify to form two series of solid solutions, with a eutectic point at 513°, and, on further cooling, a reaction takes place at 469°, a compound, $NaBr,2CaBr_2$, being formed. Sodium bromide forms simple eutectiferous systems with both strontium and barium bromides, the eutectic temperatures being 486° and 600° respectively.

Potassium bromide forms double salts with all the bromides of the alkaline earths. The compounds $2KBr,MgBr_2$ and $KBr,MgBr_2$ decompose at 348° and 391° respectively, and there is a eutectic point between them at 334°. Solid solutions are not formed in this or the following series. Only a single compound is formed with calcium bromide, $KBr,CaBr_2$, represented by a maximum on the freezing-point curve at 637°. There are eutectic points at 544° and 563° respectively. In the strontium series there are two flat maxima, $2KBr,SrBr_2$, freezing at 559°, and $KBr,2SrBr_2$, at 574°. There are thus three eutectic points, at 556°, 534°, and 562° respectively. One flat maximum at 634° occurs in the barium series, corresponding with the compound $2KBr,BaBr_2$, and the eutectic temperatures are 632° and 612°.

C. H. D.

The Dissolution of Sodium Chloride Crystals in Solutions containing Carbamide. WALTER SCHNORR (*Zeitsch. Kryst. Min.*, 1915, **54**, 289—331).—The author has carried out an exhaustive series of experiments on the manner in which a crystal of common salt dissolves when placed in an unsaturated salt solution, with particular reference to the effect of the presence of varying quantities of carbamide, which is known to influence the habit of growth of such crystals. It is found that, if growth and dissolution take place in presence of the same quantity of carbamide, sharp corners develop during solution at the poles of those faces which predominate in the growing crystal. The velocity of solution of each face is dependent on the degree of unsaturation of the solution and on the quantity of carbamide present. The differences in solution–velocity between different faces diminish as the degree of unsaturation increases, but are enhanced by increase in the quantity of carbamide, particularly with respect to the vicinal icositetrahedron and octahedron faces. The form of the final body also depends, in many cases, on the form of the crystal first placed in the unsaturated solution. E. H. R.

Polymorphism of Ammonium Nitrate. FRÉD. WALLERANT (*Bull. Soc. franç. Minéral.*, 1916, **39**, 162—163; from *Chem. Zentr.*, 1917, ii, 6).—The author maintains the correctness of his previous observations (A., 1906, ii, 152). The discrepancies between his results and those of Behn (*Proc. Roy. Soc.*, 1908, [A], **80**, 444) between 82° and −16° are probably attributable to differences in the methods of investigation, as, for example, occurrence of under-cooling. H. W.

Ammoniates of Silver Salts. III. G. BRUNI and G. LEVI (*Gazzetta*, 1917, **47**, i, 259—272. Compare A., 1916, ii, 482, 617). —The following thermochemical data have been arrived at experimentally. Molecular heats of solution in water: $AgNO_3$, −5·30 Cal. (1 gram-mol. in 1000 mols. H_2O) or −5·70 Cal. (1 gram-mol. in 1600 mols. of water); $AgNO_3,2NH_3$, −9·05 Cal.; $AgNO_3,3NH_3$, −10·44 Cal.; $AgClO_4$, −2·17 Cal.; $AgClO_4,2NH_3$, −10·71 Cal.; $AgClO_4,3NH_3$, −11·18 Cal. Heats of formation in solution: $AgNO_3 + 2NH_3 + aq. = +12·68$ Cal.; $AgClO_4 + 2NH_3 + aq. = +12·71$ Cal. Heats of formation in the solid state: $AgNO_3 + 2NH_3 = +33·64$ Cal.; $AgNO_3 + 3NH_3 = 42·94$ Cal.; $AgClO_4 + 2NH_3 = +38·40$ Cal.; $AgClO_4 + 3NH_3 = +47·77$ Cal. (compare Berthelot and Delépine, A., 1899, ii, 748).

These results indicate that only the diammoniates exist in solution. The triammoniates, which exhibit considerable heats of formation in the solid state, are completely decomposed in ~~solu~~tion into the corresponding diammoniates and free ammonia.

Measurements of electromotive force indicate the existence in solution of the complex $Ag(NH_3)_2$, and of this alone, even in ammoniacal solutions of silver nitrite. The compound, $AgNO_2,NH_3$, is consequently regarded as the double salt, $AgNO_2,(AgNO_2,2NH_3)$, and a similar explanation may hold for the compound $AgNO_3,NH_3$. T. H. P.

Saturated Solutions of Potassium and Magnesium Sulphates. H. S. van Klooster (*J. Physical Chem.*, 1917, **23**, 513—518).—Van't Hoff has indicated that polyhalite,

$$Ca_2MgK_2(SO_4)_4,2H_2O,$$

can co-exist in equilibrium at 25° with any two of the following substances: syngenite, $CaK_2(SO_4)_2,H_2O$; reichardtite,

$$MgSO_4,7H_2O;$$

and gypsum, $CaSO_4,2H_2O$. He suggests that at some temperature below 25° polyhalite will break up into the three above-mentioned salts. The present author has undertaken to investigate this point, and, having found not inconsiderable discrepancies in the work of Basch (*Diss., Berlin*, 1901), he has as a preliminary redetermined the solubility curve of potassium magnesium sulphate at 25°. The experimental details are given in the paper, and it is especially pointed out that the conclusions of van't Hoff, which are based on the determinations of Basch, are of questionable accuracy. J. F. S.

Phosphorescent Zinc Sulphide. (Miss) Elizabeth MacDougall, Alfred Walter Stewart, and Robert Wright (T., 1917, **111**, 663—683).—An investigation in which the nature and cause of the phosphorescence of zinc sulphide are examined. It is shown that pure zinc sulphide, prepared in various ways, can be obtained in a phosphorescent condition. The addition of certain impurities has a marked effect, in some cases, as with iron, inhibiting the action, and in others, for example, manganese, altering the tint of the phosphorescence. The presence of a chloride always improves the phosphorescence. The temperature to which the preparation has been heated has the greatest influence on the phosphorescence. This temperature may be varied within limits, but in general the best results are obtained at temperatures between 650° and 900°. Washing, rubbing, or disturbing the final product in any way tends to diminish its phosphorescent power. Amorphous zinc sulphide is non-phosphorescent, and the crystalline variety does not give such marked effects as the semi-crystalline samples. The phosphorescence of specimens of zinc sulphide made from salts containing no chloride is not so brilliant as that of specimens produced in the presence of chlorides. The experiments show that phosphorescence is much influenced by physical conditions, and cannot be regarded as entirely due to the chemical nature of the phosphorophore. Thus it is established that the strongest phosphorescence is observed in specimens which are just on the border between the amorphous and crystalline conditions, and this state can be attained either by heating for a very short period at a high temperature or for a longer period at a lower temperature. The fact that washing diminishes the phosphorescence indicates the probable presence of some material which has a strong influence on the phenomenon. Since crushing, grinding, or rubbing of the final product also decreases the phosphorescence, it seems probable that the supposed impurity forms a skin over the particles of the sulphide, which is removed by washing or disintegrated by mechanical treatment. It appears from the evidence that the chloride ion may be the cause of the enhanced phosphorescence due to impurity. This may act in the following way: When the impure sulphide is heated, the chloride reacts with it and produces a surface film of zinc chloride on the sulphide, and this film, on cooling, may contract and produce a strained condition of the material within the film. The effect of additional impurities would be to influence the fusibility of the sulphide and chloride, and it may be in this action that the main influence of the impurities is to be sought. J. F. S.

The Solubility of the Salts of Isotopic Elements. K. Fajans and J. Fischler (*Zeitsch. anorg. Chem.*, 1916, **95**, 284—296).—On the assumption that saturated solutions of corresponding salts of isotopic elements must contain the same number of molecules in equal volumes, it follows from the different molecular weights that the solubilities expressed in grams per litre and the densities should be different. This has been tested by means of lead nitrate prepared from ordinary lead of atomic weight 207·15 and lead from carnotite with atomic weight 206·59 (Richards and Lembert, A., 1914, ii, 653), the nitrates being purified by repeated recrystallisation in platinum vessels. The determinations of solubility are made in Jena-glass vessels in a thermostat constant to 0·02°, equilibrium being reached from both sides, for which two days are necessary. Direct analytical determinations of the lead in the two solutions give results which differ by less than the possible error, but the more exact method of determining the density of the solutions shows that there is a real difference, ordinary lead nitrate being the more soluble, but the values differ by less than 0·1% (compare A., 1915, ii, 207). C. H. D.

A Method for the Relative Atomic Weight Determinations of Isotopic Elements. K. Fajans and M. Lembert (*Zeitsch. anorg. Chem.*, 1916, **95**, 297—339. Compare preceding abstract). —If saturated solutions of the nitrates of two lead isotopes contain the same number of molecules per litre, which is the case if the ratio of molecules of salt to molecules of water is the same, the molecular volumes being identical and the change of volume on solution also the same, the relative atomic weights may be determined from measurements of the solubility. The difference in weight between equal volumes of the two solutions is in the same ratio to the mean lead content as the difference of atomic weight to the mean atomic weight.

An electrically heated thermostat is used, the mercury contact of the regulator being provided with a small automatic hydrogen generator to prevent fouling of the mercury. The temperature is maintained at 24·45°±0·002°. One end of the improved pyknometer is closed with a tap and the other with a narrow, ground-on tube. In all cases at least three days are allowed for the attainment of equilibrium. The nitrates used are prepared from ordinary lead (atomic weight 207·15), carnotite lead (206·59), and lead from Joachimsthal pitchblende (206·57), all being repeatedly recrystallised, the removal of nitric acid being specially important. The following values are found for $D_4^{24\cdot45}$: ordinary lead nitrate, 1·444499 ± 0·000013; carnotite lead, 1·443587 ± 0·000016; pitchblende lead, 1·443586 ± 0·000015. The molar solubilities are, within the experimental error, identical. The values for the difference in weight of 10 c.c. of the two saturated solutions are: for ordinary and carnotite lead, 9·04 ± 0·26 mg., and for ordinary and pitchblende lead, 9·35 ± 0·52 mg., the values found experimentally being respectively 9·12 ± 0·29 and 9·13 ± 0·28 mg. The agreement is sufficiently close to justify the use of the method for determining relative atomic weights.

The definition of an element is discussed in relation to these and similar observations. C. H. D.

Sodium-Lead Compounds in Liquid Ammonia Solution. F. Hastings Smyth (*J. Amer. Chem. Soc.*, 1917, **39**, 1299—1312).—The nature of the compounds which are formed when metallic lead is dissolved in liquid ammonia containing sodium has been investigated by electrolysing the solutions with a platinum gauze anode and a lead cathode. Measurements of the gain in weight of the anode and the loss in weight of the cathode were made in a series of experiments with solutions which had been previously saturated with lead. The results show that 2·26 gram-atoms of lead are deposited at the anode and dissolved at the cathode for each faraday passed through the solution. This value is independent of the concentration of the solution between the limits of 0·01 and 0·1 mol. of sodium per litre, and is also independent of the magnitude of the current.

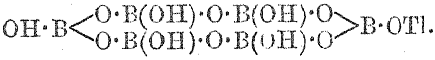
Measurements of the solubility at −33° of lead in liquid ammonia containing varying amounts of sodium show also that more than two atoms of lead are dissolved for each atom of sodium present.

The electrolytic and solubility data lead to the conclusion that the solutions examined contain an equilibrium mixture of electrolytes of the formulæ $NaPb_2$ and $NaPb_3$. If these are equally ionised, the value of the ratio $[Pb_3']/[Pb_2']$ is about 0·36.

The compound containing the larger proportion of lead is more soluble in liquid ammonia than the other, and has not been isolated. When the solutions are evaporated, the vapour pressure falls until solids begin to separate, when the pressure remains constant until the solvent has completely disappeared, when it falls to zero. The deposited solid is not therefore an ammonia compound. H. M. D.

The Crystal Structure of the Compound $H_{10}Tl_2B_{12}O_{24}$. Rudolf Scharizer (*Zeitsch. Kryst. Min.*, 1914, **54**, 232—237).—A fresh examination of the crystals of this thallium borate, prepared by Buchtala (A., 1914, ii, 135), shows it to be monoclinic [$a:b:c=1\cdot5827:1:1\cdot9546$; $\beta=94°25'$]. The crystals form curious twins, which have been examined goniometrically and optically.

Buchtala gives to this compound the formula $Tl_2B_{12}O_{19},5H_2O$, but the author considers that the water is probably water of constitution, not water of crystallisation. The formula then becomes $2(H_5TlB_6O_{12})$, and may be written



$$\mathrm{OH{\cdot}B}\left<\begin{matrix}\mathrm{O{\cdot}B(OH){\cdot}O{\cdot}B(OH){\cdot}O}\\ \mathrm{O{\cdot}B(OH){\cdot}O{\cdot}B(OH){\cdot}O}\end{matrix}\right>\mathrm{B{\cdot}OTl}.$$

The further series of thallium borates prepared by Buchtala, $Tl_2B_2O_4,H_2O$, $Tl_2B_4O_7,2H_2O$, $Tl_2B_6O_{10},3H_2O$, $Tl_2B_8O_{13},4H_2O$, may be regarded as an homologous series of the general formula $Tl_2O[HBO_2]_{2n}$, in which the boron atoms, linked together by oxygen atoms, form a chain, for example,

$$\mathrm{Tl{\cdot}O{\cdot}B(OH){\cdot}O{\cdot}B(OH){\cdot}O{\cdot}Tl}.$$

E. H. R.

The System Iron–Copper. Rudolf Ruer and Franz Goerens (*Ferrum*, 1916, **14**, 49—61; from *Chem. Zentr.*, 1917, i, 1065. Compare Ruer and Fick, A., 1914, ii, 274).—With the object of elucidating certain discrepancies, particularly in regard to the behaviour of the molten metals, the authors have melted electrolytic copper and iron (m. p. 1528°) in porcelain tubes in an atmosphere of nitrogen, and have investigated the alloys thermally, micrographically, and magnetically. A separation of layers actually occurs when the pure metals are melted together. On the other hand, that portion of the freezing-point curve which lies between the end-points of the mixture gap (24% Cu at 1450° and about 85% Cu at 1375°) is definitely shown not to be horizontal; the observed discrepancy cannot be attributed to under-cooling. On solidification, therefore, the system Fe–Cu shows the behaviour of a system of three or more substances. The absorption of impurities during the process of melting, in amount sufficient to explain the phenomena, could not be established. It must therefore be assumed that a molecular complex is formed which, on account of its slow velocity of production and decomposition, plays the part of a third substance, but further confirmation of this view was not obtained. Apparently an inexplicable contradiction of the phase rule is here presented. For further details, the tables and diagrams of the original communication must be consulted.

H. W.

A Colourless Modification of Mercuric Iodide. G. Tammann (*Nach. K. Ges. Wiss. Göttingen*, 1916, 292—293; from *Chem. Zentr.*, 1917, i, 1065).—If mercuric iodide is heated at about 300—500° in a long glass tube, one end of which is connected to a receiver in which the pressure can suddenly be decreased from 1 to 1/10th atmosphere, it condenses in the form of a colourless snow, which becomes pink in a few seconds and red after some minutes. The existence of such a colourless modification corresponds with the analogy between mercury and cadmium and zinc in the periodic system. H. W.

Decomposition of Cerous Oxalate in a Reducing or Inert Atmosphere and a New Property of the Higher Oxides of Cerium. WALLACE S. CHASE (*J. Amer. Chem. Soc.*, 1917, **39**, 1576—1582).—By heating cerous oxalate at 550° in an atmosphere of hydrogen or nitrogen, a bluish-black, amorphous substance is obtained which consists of a mixture of the oxides CeO_2 and Ce_4O_7 and free carbon. When the decomposition has been carried out in an atmosphere of hydrogen, the residue takes fire when brought in contact with the air. The phenomenon is attributable to the oxidation of hydrogen, which is adsorbed in large quantities by the mixture resulting from the thermal decomposition of the cerous oxalate. Other gases are also adsorbed in marked degree by the oxides of cerium which are produced in this reaction. H. M. D.

The Changes in Physical Properties of Aluminium with Mechanical Work. II. Specific Heats of Hard and Soft Aluminium. F. J. BRISLEE (*Trans. Faraday Soc.*, 1916, **12**, 57—62. Compare A., 1913, ii, 963).—Aluminium containing 0·4% of impurities has been examined in the form of square bars, drawn rod, and wire drawn until any further attempt at extension results in fracture. The specific heat is then determined for each specimen by means of a water calorimeter. The following values are found for the annealed metal: between 20° and 300°, 0·2354 ± 0·00033; between 20° and 200°, 0·2240 ± 0·0004. The hard, brittle wire gives the value 0·2220 for the range 20—100°, but this becomes less after heating for days or weeks at 100°, the tensile strength diminishing at the same time and the brittleness disappearing. C. H. D.

Constitutional Relation of Ultramarines with other Silicates. LAURENZ BOCK (*Zeitsch. angew. Chem.*, 1917, **30**, i, 161—164).—The author gives the results of a long series of experiments, which have extended over several years, in which various silicates have either been boiled with an aqueous solution of sodium or potassium sulphide or polysulphide, or else the dry substances have been heated together. The silicates investigated included precipitated silicic acid, sodium silicate (water-glass), kaolin, various zeolites, silicates of the nephelin group, etc.

Some of the conclusions arrived at are that the ultramarines should be considered as aluminium silicates analogous to the zeolites, in common with which they possess the property that the alkali bases can be replaced by other bases. Ultramarines are formed from the zeolites by replacing water by sulphide, from which it follows that the water in the zeolites is chemically combined. Silicates of different constitution, but with similar alumina–silica ratios, the so-called alumina double silicates, for example, sodalite, and analcime, give a partial formation of ultramarine, owing to the action of the alkali giving rise to some alumino-silicate (Aluminatsilicat). Silicates of the nephelin group also give rise to the partial formation of ultramarine, but generally only after deep-lying changes in the constitution have taken place. Ultramarines in which sodium is replaced by other bases cannot be prepared directly, but only by substitution methods. Ultramarine-violet and ultramarine-red are not definite chemical individuals; the violet is a transition stage to the red, which, as far as the constitution of the silicate is concerned, is totally different from the original ultramarine-blue.

The natural formation of hauyn and lapis lazuli has probably taken place in a similar way to that in which the weakly coloured ultramarines are obtained in the laboratory from minerals allied to the zeolites. T. S. P.

Alloys of Manganese with Gold. L. Hahn and S. Kyropoulos (*Zeitsch. anorg. Chem.*, 1916, **95**, 105—114).—Gold and manganese, the latter containing 5% of aluminium as well as other impurities, are heated together in nitrogen, the fusion being kept for as short a time as possible at 1300° before determining the cooling curve, as otherwise the sheath of the thermocouple is rapidly corroded. In all cases a temperature interval has been observed during freezing. Even in the case of the pure metals this amounted to 5° for gold and 17° for manganese. The freezing-point curve of the series has a maximum at 50 atomic %, with minima at 33 and 75 atomic % of gold respectively. The crystals exhibit cores, but form only a single solid solution. They do not become homogeneous on alloying for five hours at 700°, or one hour at 1000°. The hardness falls with the addition of gold, reaching a minimum at the first minimum freezing point. It then increases slightly up to the maximum on the freezing-point curve and then falls regularly. The thermal and hardness results are not in accordance with those obtained by Parravano (A., 1915, ii, 690).

Boiling the alloys with water leads to the formation of manganese dioxide. The same result occurs with 20% hydrochloric acid, so that chlorine is liberated and gold passes into solution, but is reprecipitated as long as manganese remains. The curves for the ratio of dissolved and undissolved manganese approach more nearly to the form required by Tammann's theory (A., 1915, ii, 427) as the time of action is increased. C. H. D.

The Carburation of Iron by Alkali Cyanides and Cyanates. A. Portevin (*Compt. rend.*, 1917, **165**, 180—182. Compare A., 1915, i, 944).—Working with mixtures of potassium cyanide and cyanate in varying proportions, and at temperatures from 750—900°, the time of heating being two or four hours, the author finds that the maximum carburation of iron is not attained when potassium cyanide alone is used, but when the mixture contains from 25—40% of potassium cyanate. W. G.

The Tempering of Steel. HENRY LE CHATELIER (*Compt. rend.*, 1917, **165**, 172—174).—The author considers that the work of Portevin (compare this vol., ii, 372), Chevenard (compare this vol., ii, 414), and Dejean (compare following abstract) affords experimental proof of the theory of tempering put forward by André Le Chatelier (compare *Bull. Soc. Encouragement*, 1895, 1340). W. G.

The Formation of Troostite and Martensite. P. DEJEAN (*Compt. rend.*, 1917, **165**, 182—185).—With a rapid tool steel containing 18% of tungsten and 4% of chromium, varying the initial temperature of cooling, but not the velocity of cooling, the cooling curves show a thermal critical point, *A*, at from 800° to 700° when the initial temperature of cooling varies from 850° to 900°. When the initial temperature of cooling passes 900°, a second point, *B*, appears at a little above 400°, and at an initial temperature of 980° the point *A* has completely disappeared. Similar phenomena have been obtained with a large number of steels, particularly the "self-tempering" steels, by suitably modifying the temperatures of heating and the velocities of cooling. Those steels which show the point *A* are found to contain perlite or troostite, those which show the point *B* martensite, and those which show both *A* and *B* are composed of troostite and martensite. Working with carbon steels and varying the velocities of cooling, the author finds that between 700° and 500° they show a point analogous to *A*, and at lower temperatures ($< 200°$) a point which is probably related to *B*.

There is no discontinuity between the point of formation of perlite and that of troostite, these two constituents being formed of an aggregate of ferrite and cementite, the perlite containing almost all the carbon of the steel, the troostite only a portion. Below the point *A*, the carbon remaining in solution in the iron round the troostite maintains it in the form of austenite, until at the point *B* this is transformed into martensite. In order completely to suppress the formation of troostite and obtain pure martensite, with a given velocity of cooling it is necessary to pass the critical point of heating by an amount which is greater in proportion as the velocity of cooling is slower. W. G.

The Classification of Nickel Steels and Manganese Steels. P. DEJEAN (*Compt. rend.*, 1917, **165**, 334—337).—The nickel steels containing less than 25% of nickel, which are said to be irreversible, should really be divided into two classes, namely: (1) the perlitic steels with 0—10% of nickel, which are pseudo-reversible; (2) the martensitic steels containing 10—25% of nickel, which constitute the true irreversible steels. The same holds good for low carbon, manganese steels. Steels containing 0—3·5% of manganese are perlitic and give the point *A*; those containing from 3·5—11% of manganese are martensitic and give the point *B*. There is also an intermediate zone at 3·5—4% manganese in which the steels have the two points *A* and *B*, and are formed of troostite and martensite. As the carbon content rises to 0·7—1·0%, this intermediate zone becomes of considerable importance. With equal manganese content, the temperature of point *A* rises and that of point *B* falls, and finally, by suitable cooling, it is possible to produce the point *A* in steels for which the point *B* is below 0°. Thus steels with troostite and austenite are obtained. W. G.

Studies in Alloys Resistant to Sulphuric Acid by Improvement of the Resistance of Nickel. ROLAND IRMANN (*Metall und Erz.*, 1917, **14**, 21—30, 37—42; from *Chem. Zentr.*, 1917, i, 1069—1070. Compare A., 1916, ii, 530).—On the assumption that metallic alloys behave towards acids and other electrolytes as aggregates of small galvanic cells the poles of which are formed by the constituents of the alloy, it is possible to obtain information regarding the behaviour of the alloy by the study of cells composed of its constituents. If the cell Ni,Cu,H_2SO_4 (50° Bé.) is short-circuited at 90°, the copper is unattacked and nickel dissolved; the potential sinks rapidly from 0·55 to 0·25 volt. The same is true for other combinations of elements, one component being invariably unprotected. Stable alloys are only to be expected when new constituents appear either as mixed crystals or chemical compounds.

Nickel–Copper.—The series of alloys (uninterrupted series of mixed crystals) shows a maximal resistance to sulphuric acid (50° Bé., 95°) at 50%; nickel is almost exclusively dissolved.

Nickel–Tungsten–Copper.—The three metals cannot be alloyed in all proportions. With increasing tungsten content, the receptivity for copper diminishes. Four alloys have been prepared containing respectively 2·11% W, 48·70% Cu; 3·22% W, 36·25% Cu; 5·12% W, 42·26% Cu; 9·57% W, 39·28% Cu. Formation of layers only occurred in one instance, the compositions being 2·23% W, 66·88% Cu, and 5·80% W, 45·10% Cu. The ternary alloy is far more stable towards acid than the nickel–tungsten alloy, particularly when containing 2% W, 20% Cu; 5% W, 45% Cu, or 10% W and 15% Cu. It has a high electrical resistance; the smallest value observed was higher than that of constantan, whilst the highest was as great as that of the best resistance material (except chromium–nickel). The strength of the moulded alloys is very considerable. The alloys can be readily rolled, those which are most resistant to acid being the best in this respect. An increase in the tungsten content would probably cause increased stability towards acid and higher electrical resistance.

Nickel–Tungsten–Copper–Iron.—The alloys were prepared by adding increasing quantities of iron wire (up to 10%) to the Ni–Cu–W alloy (*circa* 44% Cu and 3·9% W). Slight separation occurred with slow cooling. The stability towards sulphuric acid (50° Bé.) increases markedly with increasing iron content (2—10 times); traces of nickel, but neither iron nor copper, pass into solution. With more concentrated acid, corrosion is more pronounced. The mechanical properties are greatly improved by the addition of iron, but the electrical resistance is scarcely affected. The favourable behaviour of alloys containing iron enables ferrotungsten to be used instead of the expensive tungsten.

Copper–Nickel–Zinc–Tungsten.—If tungsten (1—3%) is added to Cu–Ni–Zn alloy, a separation occurs; the upper layer contains Ni–Cu–Zn, rich in copper; the lower consists of Ni–W or Ni–W–Cu, rich in tungsten. Only small quantities of tungsten (up to 0·39%) could be brought into the alloy by addition of Cu–Zn to Ni–W. No improvement could be effected in the stability of the Cu–Zn–Ni alloy towards acid, all the specimens being powerfully attacked and covered with a layer of sulphate. H. W.

Action of Metaphosphoric Acid on the Oxides of Molybdenum. A. COLANI (*Compt. rend.*, 1917, **165**, 185—187).—When molybdenum trioxide is heated with metaphosphoric acid to a dull red heat, it undergoes a very slight reduction, the loss in oxygen corresponding with the formation of the hypothetical oxide Mo_6O_{17}. When molybdenum dioxide is similarly heated, it yields the lower oxide Mo_2O_3, which gives the metaphosphate, $Mo_2O_3,3P_2O_5$, and a higher oxide, which under the experimental conditions remains dissolved in the metaphosphoric acid. W. G.

New Sulphides of Molybdenum. F. MAWROV and M. NIKOLOV (*Zeitsch. anorg. Chem.*, 1916, **95**, 188—193).—*Molybdenum pentasulphide*, Mo_2S_5, is obtained in a hydrated form by reducing a solution of ammonium molybdate, containing more than 20% of sulphuric acid, with zinc, until the colour is dark red, and then diluting, filtering, and saturating with hydrogen sulphide. The precipitate is collected and washed with hot water and then with alcohol. It is then shaken repeatedly with carbon disulphide, washed with ether, and dried at 68—75°. Analysis gives the composition $Mo_2S_5,3H_2O$. One molecule of water is lost at 135—140°, but further heating causes decomposition.

The hydrated sulphide dissolves in warm solutions of alkali sulphides to bright red solutions, depositing an orange precipitate on cooling. It dissolves with difficulty, but completely, in warm, concentrated hydrochloric acid.

Careful heating in carbon dioxide gives the anhydrous sulphide, Mo_2S_5, which is almost black. When the hydrated compound is heated in hydrogen sulphide, an exchange of water for hydrogen sulphide takes place, and the compound $2Mo_2S_5,3H_2S$ is formed. C. H. D.

Atomic Weight of Zirconium. FRANCIS P. VENABLE and JAMES M. BELL (*J. Amer. Chem. Soc.*, 1917, **39**, 1598—1608).—The value of 90·6 adopted by the International Committee for the atomic weight of zirconium is obtained by a more or less arbitrary combination of the results obtained in nine previous determinations. These results show considerable divergence, and in the authors' opinion little dependence is to be placed on any of the values, since it is very probable that the methods employed involve errors other than those which may be described as accidental. The oxide is involved in most of these determinations, and the loss of this on ignition represents an inherent source of error the effect of which is to give a value for the atomic weight of zirconium which is less than the true value. In the experiments described, the atomic weight is based on the determination of the ratio $4Ag:ZrCl_4$.

Zirconium hydroxide was dissolved in concentrated hydrochloric acid and the oxychloride separated by crystallisation. This was then recrystallised from hydrochloric acid some forty times, and then several times from water in quartz vessels. The oxide obtained from the oxychloride was then heated at 450—500° in a current of chlorine which had been passed through carefully purified and dried carbon tetrachloride, and by a process of fractional sublimation the last traces of iron were removed. The nephelometric determination of the ratio $4Ag:ZrCl_4$ gave a mean value of 91·76 for the atomic weight of zirconium, which is more than one unit higher than the present accepted value. The authors consider that the error in their determination is not greater than 0·1.

Attempts to determine the atomic weight from the ratio $ZrCl_4:ZrO_2$ gave a mean of 92·1, but this is admittedly too high on account of the retention of chlorine by the oxide.

The density of zirconium chloride was found to be 2·803 and of the oxide 5·49. H. M. D.

Fusion of Zirconium Dioxide and the Preparation from it of Apparatus. Emil Podszus (*Zeitsch. angew. Chem.*, 1917, **30**, i, 17—19).—Zirconium dioxide, on account of its resistance towards acids and alkalis, its small conductivity for heat, its small coefficient of expansion, and its resistance to the action of heat, should be a very suitable substance for making chemical apparatus, but hitherto the results have not been satisfactory, cracks readily developing in the finished articles. The author has now found that if the zirconium dioxide is first melted in a special arc furnace and the solidified fusion then finely ground, the powder so obtained can be used for making apparatus similar to porcelain ware, which apparatus is perfectly sound and does not develop cracks. Preliminary fusion seems to be a necessary condition for obtaining sound apparatus, although the solidified fusion is crystalline and not amorphous. The fused mass is not transparent, and is broken up and powdered only with great difficulty.

Fused zirconium dioxide has D 5·89 and a hardness between that of quartz and corundum. Three determinations of the m. p. gave 2950°, 2950°, and 3000°, the last temperature being obtained with a very pure product; impurity to the extent of ½% will lower the m. p. by 100°. When pure, it is practically white in colour, but generally it is coloured yellow, since it readily takes up traces of iron; also, if slight reduction of the pure oxide takes place, a yellow colour is produced.

A special furnace is described, made of the fused oxide, in which it was possible to obtain temperatures of 2400—2500°, using coal gas and oxygen for heating. The possibility of obtaining temperatures up to 3000° in the middle of such a furnace is indicated.

T. S. P.

Tantalum Chloride with Reference to its Use in the Determination of the Atomic Weight of Tantalum. George W. Sears (*J. Amer. Chem. Soc.*, 1917, **39**, 1582—1587).—Experiments made with carefully purified tantalum chloride show that it is quite stable in an atmosphere of dry nitrogen or air, that it does not occlude chlorine, but that it undergoes hydrolysis in an atmosphere which has not been thoroughly dried by means of phosphoric oxide. On account of the readiness with which hydrolysis occurs, the author considers that tantalum chloride is not suitable for use in atomic weight determinations. H. M. D.

The Properties of Solid Solutions of Metals and of Intermetallic Compounds. F. C. Thompson (*Trans. Faraday Soc.*, 1916, **12**, 23—29. Compare A., 1916, ii, 601; Desch, A., 1915, ii, 561).—Considering the similarity of the properties of a metal in the cold-worked condition and in solid solution, crystalline distortion may be assumed to be present in both cases. In a solid solution, the distortion is due to an attempted equalisation of the atomic volumes of the metals crystallising together. The stress may be calculated from the two atomic volumes and the coefficients of cubical expansion of the components. A calculation for an alloy containing atomic proportions of gold and silver shows that the values obtained are of the right order. The theory leads to a parabolic curve for the hardness of a series of solid solutions, with a maximum at equal atomic proportions. The hardness and fragility of intermetallic compounds are similarly explained. C. H. D.

Preparation of Colloidal Gold Solutions by the Nucleus Method. Josef Reitstötter (*Koll.-Chem. Beihefte.*, 1917, **9**, 221—258).—According to Zsigmondy (A., 1906, ii, 679), it is possible to bring about an increase in the size of colloidal particles of gold by adding a small quantity of a colloidal solution to a solution of a gold salt in presence of a suitable reducing agent. Under favourable conditions, no new particles are formed, but the reduced gold is deposited on the particles already present.

This method has been further investigated, and it has been found that deep red colloidal solutions may be obtained by inoculation of an acid or slightly alkaline solution of gold chloride and reduction by means of hydrazine or hydroxylamine. The number of colloidal particles in the resulting solution is proportional to the number of nuclei in the sol used for inoculation.

By this method of increasing the size of the colloidal particles, it is possible to ascertain the number of amicroscopic particles in a given colloidal solution.

Previous observations have shown that colloidal gold particles of the smallest size are obtained by the use of an ethereal solution of phosphorus as reducing agent. Systematic attempts to ascertain the conditions favourable to the formation of the most finely divided sol have shown that particles less than 2—3·5 $\mu\mu$ cannot be obtained by this method. Incidentally, the influence of foreign substances on the spontaneous formation of colloidal gold and on the rate of increase in size of the particles has been examined.

H. M. D.

Platinum and Illuminating Gas. F. Mylius and C. Hüttner (*Zeitsch. anorg. Chem.*, 1916, **95**, 257—283).—When a luminous coal-gas flame comes in contact with platinum, a black layer is formed, and after the carbon has been burnt off in air the metal is left in a rough and brittle state, without loss of weight. The influence of different metallic impurities is examined by heating pieces of foil in Jena-glass tubes in a stream of coal gas under comparable conditions. The action is greatly increased by the presence of iron or rhodium in the platinum, iridium having less effect. Of the pure metals, rhodium has the greatest effect, followed by palladium, iridium being much less active.

When a thin jet of luminous gas flame plays on a platinum surface, concentric black rings are formed, the position of which corresponds with the different zones of the flame. Synthetic coal gas, composed of methane, ethylene, carbon monoxide, and hydrogen, is without action on pure platinum or platinum-iridium, but blackens commercial platinum. The introduction of a small quantity of carbon disulphide or sulphur dioxide causes blackening. Iridium powder, heated gently in a stream of coal gas saturated with carbon disulphide, causes the formation of a black mass containing carbon and sulphur many times the weight of the iridium. Rhodium takes up sulphur from carbon disulphide even at 100°, and the corrosive action of coal gas on commercial platinum is distinctly traced to the presence of carbon disulphide in the gas. When a sufficient quantity of oxygen is present, as in the Bunsen flame, the action of sulphur and carbon is suppressed, and the corrosion which takes place is due to oxygen, and is very small for pure platinum, but is increased by the presence of iron or iridium (compare Burgess and Waltenberg, A., 1916, ii, 442).

C. H. D.

Rhodium. A. Gutbier and A. Hüttlinger (*Zeitsch. anorg. Chem.*, 1916, **95**, 247—252).—Rhodium begins to react with chlorine at 250°, forming the trichloride, $RhCl_3$. Bromine begins to react at the same temperature, but the product varies in composition, suggesting that the tribromide, $RhBr_3$, is formed and again dissociates.

C. H. D.

The Action of Oxygen on Rhodium. A. GUTBIER, A. HÜTTLINGER and O. MAISCH (*Zeitsch. anorg. Chem.*, 1916, **95**, 225—246).—When rhodium is heated in air or oxygen at temperatures from 600° to 1000°, the product is always the oxide, Rh_2O_3, the rate of oxidation increasing rapidly with the temperature. Above 1150°, the oxide is completely decomposed, the metal being obtained. The oxide, Rh_2O_3, is greyish-black. The previously recorded formation of lower oxides is due to incomplete oxidation.

C. H. D.

The Oxides of Ruthenium. A. GUTBIER [with G. A. LEUCHS and H. WIESSMANN] (*Zeitsch. anorg. Chem.*, 1916, **95**, 177—187. Compare A., 1905, ii, 534).—Ruthenium tetroxide reacts explosively with even very dilute alcohol. By using dilute aqueous solutions and taking only small quantities for each operation, a brown or black colloidal product may be obtained which may be evaporated on the water-bath. The residue does not yield constant figures either for water or oxygen. Heating in air or oxygen forms the dioxide, RuO_2. Alcohol and potassium ruthenate also yield an indefinite product, and similar mixtures are obtained from hydrogen ruthenichloride and alkali hydroxide, and from potassium ruthenate and nitric acid. C. H. D.

The Action of Selenic Acid on Osmium. KARL HRADECKY (*Österr. Chem. Zeit.*, [2], **20**, 43; from *Chem. Zentr.*, 1917, i, 949).—Cold selenic acid has no appreciable action on osmium; at about 120°, however, the metal is dissolved to a colourless solution which contains selenious acid and osmium tetroxide, but no selenate. H. W.

Mineralogical Chemistry.

Occurrence of Native Copper in the Komandor Islands, Bering Sea. J. MOROZEWICZ (*Mem. Com. Geol. Russ.*, 1912, **72**; from *Zeitsch. Kryst. Min.*, 1915, **55**, 200—202).—Two occurrences on Copper Island are described in detail. Both are in basalt-tuff, one with associated quartz and calcite, and the other with zeolites and a small amount of calcite. The copper was the last mineral to be deposited. It is chemically pure. Staronka found by the gravimetric method 99·77, and by the electrolytic method 100% Cu. The zeolites include analcite (anal. I by Staronka), and the new species, stellerite (Morozewicz, 1909).

Zeolites are also described from volcanic-tuff débris from Rechaya Bay. Analyses by Janczewsky of II, analcite (D 2·175), and III, laumontite. The latter in a moist atmosphere or under water contains 15·26% H_2O, corresponding with the formula $CaAl_2Si_4O_{12},4H_2O$.

	SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	H_2O.	Total.
I.	55·06	23·08	—	—	14·11	8·43	100·68
II.	57·40	15·55	8·38	0·46	—	18·66	100·45
III.	52·45	22·35	12·32	0·40	—	13·79	101·31

L. J. S.

Mineralogy of the Island of Borneo. G. P. Tschernik (*Trav. Mus. Géol. Pierre le Grand Acad. Sci. St. Pétersbourg*, 1912, **6**, 49—95; from *Zeitsch. Kryst. Min.*, 1915, **55**, 184—191).—Material is described and analysed from the alluvial occurrences of platinum, osmiridium, and gold with associated diamond and other heavy minerals in the Tanah-Laut district, south-east Borneo. Ten analyses of platinum, which occurs usually as minute scales, show: Pt, 58·30—77·08; Ir, 3·06—28·87; Pd, 0·23—1·00; Rh, 0·21—3·86; Os, traces—1·78; Ru, traces—1·25; Fe, 4·19—10·83 (and in ferroplatinum 20·89); Cu, 0·22—1·19; Au, traces—3·70; Ag, traces—0·27; sp. gr. 16·68—22·12 (for the ferroplatinum 14·15). Fifteen analyses of osmiridium show: Ir, 10—70; Os, 17—80; Pt, 0·1—5; Rh, 1—11·25; Ru, traces—8·9; Pd, traces; Fe, traces—0·45; Cu, traces—0·51; sp. gr., 14·25—21·26. Twelve analyses of gold dust show Au, 62·06—90·99; Ag, 2·13—16·11; Cu, 0·03—5·32; Fe, trace—0·55; also traces of Bi, Hg, and sometimes small amounts of Pt, Ir, Pd. A gold amalgam, D 15·439, from near Pleiari gave: Au, 34·23; Hg, 60·57; Ag, 4·78; Pt, 0·12; chromite?, 0·09; total, 99·79, agreeing with the formula $2Au_2Hg_3 + AgHg$.

Analyses of the heavy minerals include: Rutile (anal. I), small crystal fragments. Topaz (II), transparent, pale yellow. Ilmenite (III), rounded grains. Chromite (IV), brownish-black grains. Ruby (V), rose-red grains, usually cloudy. Zircon, colourless crystals (VI) and brown crystals (VII).

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.
I.	0·04	96·82	—	1·84	—	trace
II.	29·23	—	61·69	—	—	—
III.	0·43	44·02	0·11	16·06	35·83	0·53
IV.	0·43	—	9·05	14·29	12·99	—
V.	—	—	99·32	0·88	—	—
VI.	33·04	—	—	0·02	—	—
VII.	34·52	trace	—	1·26	—	—

	CaO.	MgO.		Total.	Sp. gr.
I.	—	—	[Nb_2O_5 (and Ta_2O_5) 0·42]	99·12	4·51
II.	—	—	[F, 13·72 :K_2O,Na_2O, not det.]	98·86	3·54
III.	0·08	1·98		99·04	4·62
IV.	0·40	7·37	[Cr_2O_3, 54·59]	99·12	4·68
V.	—	—		100·20	3·96
VI.	trace	—	[ZrO_2, 66·14]	99·20	4·79
VII.	—	trace	[ZrO_2, 63·31]	99·09	4·56

L. J. S.

Pyrargyrite from Nagybánya, Hungary. J. LOCZKA (*Ann. hist.-natur. Mus. Nat. Hungar.*, 1911, **9**, 318—320, 320—323; from *Zeitsch. Kryst. Min.*, 1914, **54**, 185).—Analysis gave:

Ag.	Cu.	Fe.	Sb.	As.	S.	Total.	Sp. gr.
59·82	0·07	0·12	22·00	0·08	17·82	99·91	5·852

L. J. S.

Minerals from Monte Arco, Elba, Italy. E. MANASSE (*Atti Soc. Toscana Sci. Nat. Mem.*, 1912, **28**, 118—189; from *Zeitsch. Kryst. Min.*, 1915, **55**, 315—319).—A description is given of the veins of iron, manganese, lead, and copper ores and of the surrounding rocks at Monte Arco, on the east coast of the island of Elba. Thirty mineral species are described in detail; analyses are given of the following: Pyrrhotite, massive, with lamellar to granular structure, D 4·56; Fe, 59·02; S, 39·33; CaO,MgO, traces; insol. in HCl, 0·61; total, 99·56; formula Fe_5S_6. Mispickel, massive, with lamellar structure, D 5·78; Fe, 33·28; Co, 0·48; As, 46·98; S, 18·74; insol. in HNO_3, 1·49; total, 100·97. Galena, lamellar and zinciferous; PbS, 96·45; ZnS, 3·55%. Opal associated with limonite and coloured red by iron; SiO_2, 90·88; H_2O, 4·86; Fe_2O_3, 4·14; total, 99·88. Reddish-yellow, ochreous limonite contains only 12·86% H_2O, whilst the black, pitchy variety ("stilpnosiderite") contains H_2O, 14·20; Fe_2O_3, 83·16; SiO_2, 2·57; CaO,MgO, traces; total, 99·93, agreeing with the usual formula $H_6Fe_4O_9$. Apatite occurring in quartz-tourmaline veins, gave: CaO, 54·86; P_2O_5, 42·23; Cl, 0·31; F, 2·27; insol., 0·56; total (less O for F), 99·44. Tourmaline, blackish-brown crystals, gave the results under I, agreeing with the empirical formula

$$16SiO_2,4B_2O_3,9Al_2O_3,3FeO,4MgO,Na_2O,3H_2O,$$

or, in the form deduced by Penfield and Foote,

$$H_2Na_2Fe_3Mg_4Al_6(Al_3[BOH]_2Si_4O_{19})_4.$$

Ilvaite, as black, crystalline masses, gave II. Epidote, forming a compact epidosite encrusted with minute crystals of epidote, gave III. Hedenbergite is the most abundant iron silicate (anal. IV). Yellowish asbestos gave the results under V, agreeing with the tremolite formula.

	SiO_2.	Al_2O_3	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.
I.	36·09	34·43	n. d.	8·58	trace	0·53	5·60	0·35
II.	29·61	0·63	19·81	33·78	0·51	13·23	trace	—
III.	36·51	24·50	12·38	n. d.	—	24·34	0·45	—
IV.	48·05	1·61	n. d.	26·14	1·15	20·40	1·34	—
V.	54·65	1·59		—	—	14·21	25·98	0·21

	Na_2O.	H_2O.	Total.	Sp. gr.
I.	2·09	1·93	100·00*	3·12
II.	—	2·73	100·30	3·95
III.	—	1·95	100·13	3·29
IV.	—	0·68	99·37	3·50
V.	1·19	1·92	99·75	—

* Including: B_2O_3, 10·40 by difference; F, trace.

Halloysite, white, soft, and moist, is found in the magnetite and limonite masses; on drying in the air, it hardens and acquires a soap-like appearance, and then breaks with a conchoidal fracture. It is opaque, but in water becomes almost transparent, like gelatin. Optically isotropic; D 2·16, H, 1—2. Analysis of air-dried material gave: SiO_2, 39·17; Al_2O_3, 34·20; CaO, trace; H_2O, 26·72; total, 100·09. Over sulphuric acid, it soon loses 8·94% H_2O, which is reabsorbed in a moist atmosphere. At 160° 12·66% H_2O is lost, and there is no loss between 250° and 400°. At 250° the composition of the material is the same as that of kaolin, $H_4Al_2Si_2O_9$, which requires 13·91% H_2O. The water of halloysite held below this point is considered to be adsorbed water, the remainder being water of constitution. Comparative dehydration experiments were made with kaolin from Tolfa, Rome; over sulphuric acid, or up to a temperature of 400°, the loss amounts to only 0·95% of the total of 14·98% H_2O. Samoite occurring with Elba halloysite has the appearance of a hardened jelly and varies in colour, green, sky-blue, or white. D 2·08; H, 3. It is completely decomposed by hydrochloric acid with the separation of gelatinous silica. Analysis gave: SiO_2, 32·79; Al_2O_3, 34·59; CaO, 1·56; MgO, 0·50; CuO, trace; H_2O, 29·64; total, 99·08. The water is lost gradually and continuously over sulphuric acid and when heated, there being no break, as is the case with halloysite. The mineral is therefore regarded as a hydrogel or adsorption compound, and not a hydrated kaolin like halloysite. L. J. S.

Mineral Occurrences in the Worthington Mine, Sudbury, Ontario. T. L. Walker (*Econ. Geol.*, 1915, **10**, 536—542; from *Jahrb. Min.*, 1917, i, 151—152).—The ore of this mine occurs in a somewhat weathered hornblende-plagioclase-rock, and consists mainly of pyrrhotite and copper-pyrites. Embedded in it are cleavable phenocrysts, up to 5 cm. across, of pentlandite, together with nickeliferous pyrites and small amounts of polydymite, blende, niccolite, and molybdenite. Analysis I of this pentlandite leads to the formula $(Ni,Fe)_{11}S_{10}$, already deduced by Dickson. Rounded masses of pentlandite also occur in the massive pyrites, giving the ore the appearance of a conglomerate. Analysis II of this pentlandite, D 4·638, suggests that the material is mixed with a small amount of polydymite. Analysis of the pyrites gave III.

	Fe.	Ni.	Co.	Cu.	S.	CaO.	Insol.	Total.
I.	30·68	34·48	1·28	—	32·74	—	0·56	99·74
II.	27·64	32·13	0·90	0·30	34·82	1·58	0·78	98·15
III.	44·57	2·44	—	—	51·83	—	—	98·84

The author believes that this ore has not been formed by magmatic differentiation alone, but that aqueous agencies have also played a part. L. J. S.

Chemical and Mineralogical Observations. G. A. Koenig (*J. Acad. Nat. Sci. Philadelphia*, 1912, **15**, 405; from *Zeitsch. Kryst. Min.*, 1916, **55**, 409—410).—*Aurobismuthinite*, a new species from unknown locality, is light grey, soft, massive, and granular with numerous cleavage surfaces; analysis: Bi, 69·50; Au, 12·27; Ag, 2·32; S, 15·35; total, 99·44, gives the formula $(Bi,Au,Ag_2)_5S_6$.

Stibiobismuthinite from Nacozari, Sonora, Mexico, as aggregates of long, prismatic crystals with the usual cleavage and polysynthetic structure of bismuthinite, gave: Bi, 69·90; Sb, 8·12; S [diff.], 21·92%, agreeing with $(Bi,Sb)_4S_7$.

Crystalline seladonite from a basalt-tuff near Vail, Arizona, consists of minute prisms, pyramids, or scales. It is bluish in the air and pale olive-green under water. Analysis under I gives the formula $(K_2,H_2,Mg,Fe)_3(Fe_2,Al_2)(SiO_3)_6,1{\cdot}24H_2O$.

	SiO_2.	SO_3.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Insol.	Total.
I.	54·73	—	7·56	13·44	5·30	0·00	5·76	7·40	—	6·40	—	100·59
II.	—	30·47	—	50·94	—	—	—	2·02	4·20	11·73	0·69	100·01

Natrojarosite (anal. II) from a new locality, namely, San Toy Mine, Santa Eulalia, Chihuahua, Mexico, occurs with gypsum and mimetite as straw-yellow, silky aggregates of hexagonal crystals. The honey-yellow crystals of mimetite from this locality gave: PbO, 67·6; As_2O_5, 22·6; $PbCl_2$, 9·8%. L. J. S.

Chemical Constitution of Bauxite from Bihar, Hungary. B. von Horváth (*Földtani Közlöny*, 1911, **41**, 254—257, 341—343; from *Zeitsch. Kryst. Min.*, 1914, **54**, 182—183).—The bauxite deposits of the Bihar Mountains in comitat Bihar are situated on a plateau of Upper Jurassic limestone. Analyses I and II are of reddish-brown material from the neighbourhood of Vaskoh, and III of greyish-white material from Mt. Kuku, near Tizfalu. Twelve other partial analyses of the reddish-brown bauxite gave: SiO_2, 0·92—2·23; Al_2O_3, 39·32—58·60; and another partial analysis of the greyish-white gave: SiO_2, 5·55; Al_2O_3, 52·11.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	Total.
I.	1·52	3·10	53·20	27·66	0·20	trace	14·39	100·07
II.	1·52	1·95	58·26	30·22	—	0·09	8·09	100·13
III.	12·38	3·95	58·74	7·84	0·32	0·11	16·31	99·65

L. J. S.

Mineralogy of the Kyshtymsk Mountains. A. W. Nikolaev (*Trav. Mus. Géol. Pierre le Grand, Acad. Sci. St. Pétersbourg*, 1912, **6**, 171—231; from *Zeitsch. Kryst. Min.*, 1915, **55**, 182—184).—Descriptions are given of twelve mineral species and analyses of the following: Magnetite (I), granular, from Mt. Fominna. Titanomagnetite (II), as sand in the Motshalin stream. Oncosine (III, by D. S. Beljankin), resembling agalmatolite, from Borsowka. Cerolite (IV), forming the cement of a weathered serpentine "conglomerate" from the Lakejev ravine. At 125° half of the water

(9·80%) is lost. Under the microscope a gradual passage from the serpentine into the cerolite can be traced.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	0·42	0·17	—	96·74		—	—	—	—	—	97·74*
II.	1·25	4·82	5·56	68·79	19·52	—	—	—	—	—	100·78†
III.	37·42	—	38·91	1·64	—	3·31	3·55	4·88	1·24	9·00§	99·95
IV.	45·05	—	—	0·34	—	5·11	29·74	—	—	18·17	99·93‡

* Including: S, 0·003; P, 0·41; Cu, traces. † Including: MnO, 0·84. § Including: H_2O at 110°, 1·79. ‡ Including: CO_2, 1·08; SO_3, 0·44.

L. J. S.

Microchemical Reactions of Dolomite from Kielce, Poland. ST. J. THUGUTT (*Kosmos, Lemberg*, 1911, 409—417; from *Zeitsch. Kryst. Min.*, 1914, **54**, 198—199).—Eight analyses, by W. Koziorowski, of the Upper Devonian dolomites from various localities in govt. Kielce gave the extreme values under I. The ratio of $CaCO_3 : MgCO_3$ is 1 : 1, the excess of calcium present in some being due to the presence of calcite as proved by Lemberg's colour reactions with silver nitrate and potassium chromate or iron-alum. The Triassic dolomite of Suchedniow (anal. II, by W. Koziorowski) contains some aragonite. Other materials examined were: III, magnesite, from Ekaterinburg, Urals; IV, breunnerite, from Pfitsch, Tyrol; V, sideroplesite, from Heizenberg, Zell, Salzburg; VI, brown-spar, from Traversella, Piedmont; VII, colourless dolomite crystals, from Szabra, Ekaterinburg; VIII, dolomite crystals, from Snarum, Norway; IX, dolomite crystals, from Greiner, Tyrol; X, dolomite crystals, from Zabkowite, Moravia.

	CO_2	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	Insol.	Total.
I.	42·11—47·42	0·04—0·49	0·54—1·35	0·17—0·36	26·55—31·52	18·33—20·59	0·38—10·69	—
II.	40·32	1·26	2·17	1·04	26·88	15·68	13·13	100·48
III.	49·72	—	8·16	—	0·18	40·99	1·56	100·61
IV.	49·63	—	12·42	—	—	38·15	0·27	100·47
V.	40·82	—	43·29	—	—	12·89	3·00	100·00
VI.	44·47	—	11·41	—	27·55	13·99	2·73	100·15
VII.	47·07	—	2·57	—	29·89	20·38	—	99·91
VIII.	46·84	—	3·86	—	30·53	18·45	0·31	99·99
IX.	46·76	—	1·97	—	29·69	20·94	1·13	100·94
X.	47·49	—	1·79	0·25	30·03	20·84	0·05	100·45

Dolomite and magnesite, when well crystallised and containing iron, do not react with silver nitrate or iron-ammonium sulphate solution, but the Polish dolomites poor in iron give a distinct reaction at 100°. The dolomites from govt. Kielce show a strong thermoluminescence at 153° with a fine red colour. Dolomite from Fassa, Tyrol, shows a red luminescence, and calcite from Seiseralpe gives out a white light at 118—132°. L. J. S.

Malachite. Formation of Pseudomorphs. R. Ed. Liesegang (*Zeitsch. Kryst. Min.*, 1915, **55**, 264—270).—A connexion is suggested between the well-formed pseudomorphs of malachite after other minerals (cuprite, copper-glance, chessylite, etc.), and the mamillated forms so characteristic of this species. When a cube of rock-salt is placed in a concentrated solution of silver nitrate, the sodium is replaced by silver without any disturbance of the external form of the crystal. When, however, a weaker solution is employed, the surface of the cube of replaced material becomes rounded; and this rounding and irregularity of the surface increases with the greater dilution of the solution. It is therefore suggested that the mamillated forms of malachite are of pseudomorphic origin. L. J. S.

Apatite from Sunk, Styria. O. Grosspietsch (*Zeitsch. Kryst. Min.*, 1914, **54**, 461—466).—Tabular crystals of apatite, transparent with a pale brownish tinge, occur in dolomite veins in a magnesite quarry at Sunk, near Trieben. $a:c=1:0{\cdot}73341$. D 3·2057. Analysis shows it to be a very pure fluor-apatite, $CaF_2,Ca_4(PO_4)_3$, but the results agree equally well with the formula

$$4[3CaO(PO_4)_2,CaF_2]+3CaO(PO_4)_2,CaO,$$

representing a mixture of fluor-apatite and voelckerite. It is noted that many analyses of apatite give a total of more than 100%, which may be due to the presence of oxygen. Optical determinations are also given:

P_2O_5.	CaO.	MgO.	FeO.	CO_2.	F.	Ign.	Insol.	Total.
41·95	55·59	trace	0·08	present	3·02	0·23	0·02	100·89

L. J. S.

Mineralogy of Phosphorite Deposits. II. J. V. Samoilov (*Geol. Untersuch. Phosphoritlagerstätten, Moscow*, 1912, **4**, 651—671; from *Zeitsch. Kryst. Min.*, 1915, **55**, 192—193).—Experiments with plants show a difference for the phosphorites from the Gault formation as compared with those of other geological periods. Gault phosphorites from the governments Simbirsk, Saratov, and Penza, when digested with water for an hour, yielded 0·03—0·06% P_2O_5 in solution. By repeated digestion, 0·53% P_2O_5 passed into solution. Phosphorites from other geological formations do not show this reaction, nor do the Gault phosphorites from govt. Moscow and the Mangyshlak peninsula. The following are analyses by N. I. Chervyakov of Gault phosphorites from, I, Sengilei, govt. Simbirsk, and, II, from the Krutezky ravine:

	SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	K_2O.	Na_2O.
I.	33·42	4·85	2·29	0·62	28·24	1·19	1·43	1·40
II.	36·15	1·60	1·29	0·56	32·52	1·30	0·56	0·38

	P_2O_5.	CO_2.	F.	SO_3.	FeS_2.	Organic matter.	H_2O >110°.	Total (less O for F).
I.	18·21	2·40	1·68	1·48	1·55	0·69	1·91	100·65
II.	19·88	2·89	1·49	1·27	0·71	0·68	0·75	101·40

These analyses correspond with:

	$Ca_3(PO_4)_2$.	CaF_2.	$CaCO_3$.	$CaSO_4,2H_2O$.	Total.
I.	39·8	3·5	5·5	3·2	52·0
II.	43·2	3·1	6·6	2·7	55·6

Under the microscope the phosphate substance is seen to form the ground-mass in which are embedded quartz, glauconite, felspar, mica, pyrites, and organic remains; a later generation of radially-fibrous phosphate is also present. There is, however, nothing to suggest why a portion of the phosphate is soluble in water.

L. J. S.

Composition of Phosphorite Minerals. W. T. Schaller (*Bull. U.S. Geol. Survey*, 1912, **509**, 98; from *Zeitsch. Kryst. Min.*, 1916, **55**, 403).—The following formulæ are deduced from published analyses:

Dahllite	$9CaO,3P_2O_5,CaO,CO_2,H_2O$.
Francolite	$9CaO,3P_2O_5,CaF_2,CO_2,H_2O$.
Collophanite	$9CaO,3P_2O_5,CaO,CO_2,H_2O + nH_2O$.
Fluorapatite	$9CaO,3P_2O_5,CaF_2$.
Hydroxyapatite	$9CaO,3P_2O_5,CaO,H_2O$.

L. J. S.

Variscite from Sarrabus, Sardinia. A. Pelloux (*Ann. Mus. Civ. Stor. Nat. Genova*, 1912, [iii], **5**, 470—472; from *Zeitsch. Kryst. Min.*, 1915, **55**, 314).—This mineral, not previously recorded from Italy, occurs as strings and nodules in a schistose rock at Gennarella in the commune of Villaputzo. It shows a variolitic structure and conchoidal fracture. The colour is pale green to grass-green, or yellowish in more altered specimens. D 2·47; H=4. Analysis gave:

P_2O_5.	Al_2O_3.	Fe_2O_3.	H_2O.	Total.
42·27	33·29	1·71	23·11	100·38

L. J. S.

Alunite from Marysvale, Utah. B. S. Butler and H. S. Gale (*Bull. U.S. Geol. Survey*, 1912, **511**, 64; from *Zeitsch. Kryst. Min.*, 1916, **55**, 403).—Alunite has recently been found as a filling in a large crevice at this locality. It is partly fine-grained with a porcellaneous aspect (anal. I), and partly coarsely crystalline with feebly translucent crystals which show a distinct cleavage (anal. II, by W. T. Schaller):

	Al_2O_3.	Fe_2O_3.	SO_3.	P_2O_5.	K_2O.	Na_2O.	H_2O (< 110°).	H_2O (> 110°).	SiO_2.	Total.
I.	34·40	trace	36·54	0·50	9·71	0·56	0·11	13·08	5·28	100·18
II.	37·18	trace	38·34	0·58	10·46	0·33	0·09	12·90	0·22	100·10

L. J. S.

Constitution and Genesis of Iron Sulphates. IX. Voltaite from Szomolnok, Hungary. Rudolf Scharizer (*Zeitsch. Kryst. Min.*, 1914, **54**, 127—147. Compare A., 1913, ii, 715).—A specimen from Szomolnok consists of black, crystalline voltaite with a few pale brown grains of szomolnokite (J. A. Krenner, 1891). A microchemical analysis of the latter, made on a few milligrams by J. Donau, gave the results under I leading to the formula $FeSO_4,H_2O$. Ferropallidite from Chili (A., 1903, ii, 555) is identical with szomolnokite.

	SO_3.	Fe_2O_3.	Al_2O_3.	FeO.	ZnO.	CuO.	MgO.	NiO.	K_2O.	Na_2O.	H_2O.	Total.
I.	45·66	7·43	—	34·46	—	—	—	—	—	—	12·45	100·00
II.	46·78	13·47	1·58	14·07	1·69	0·55	0·48	0·08	4·73	0·50	15·70	99·73

The voltaite (anal. II) gives the formula $R_3''R_2'''(SO_4)_6,9H_2O$, when the K_2O is reckoned as $R''O$. This and previous analyses give the ratios for $R_2O:RO:R_2O_3:SO_3:H_2O$ between the extremes 1 : 2 : 1 : 8 : 12 and 1 : 6 : 1 : 8 : 12. The curve plotting the temperature and loss of water commences at 200° and shows a break at 270°, at which point about $7H_2O$ is lost.

An aqueous solution of the voltaite deposits crystals of metavoltine, but in the presence of free sulphuric acid sphæro-crystals and composite pseudo-cubic crystals of voltaite are deposited; of these a detailed description is given. L. J. S.

Ilsemannite, Hydrous Sulphate of Molybdenum. Waldemar T. Schaller (*J. Washington Acad. Sci.*, 1917, **7**, 417—420; *Chem. News*, 1917, **116**, 94).—The composition of this secondary molybdenum mineral, which is readily soluble in cold water to a deep blue solution, has previously been assumed to be $MoO_2,4MoO_3$. Material occurring disseminated through rock at Ouray, Utah, gave for the portion soluble in cold water:

MoO_3.	MoO_2.	FeO.	SO_3.	[Insol.]	H_2O.	Total.
2·37	trace	0·99	2·64	[90·50]	[3·50]	100·00

Deducting the iron as melanterite, these results lead to the formula $MoO_3,SO_3,5H_2O$. Examination of material from other localities also proves that the material is a sulphate, and is always associated with iron sulphate. Suggestions are made regarding the origin of ilsemannite by the alteration of molybdenite, jordisite, wulfenite, and molybdosodalite. L. J. S.

Crystallised Ferric Orthoarsenate. B. Ježek and A. Šimek (*Rozpr. české Akad. Prag*, 1911, **20**, No. 16, 1—6; from *Zeitsch. Kryst. Min.*, 1914, **54**, 188—189).—In the Deacon process for the manufacture of chlorine, at Hruschau, in Silesia, there are formed on the clay balls numerous black, prismatic crystals with adamantine lustre of ferric orthoarsenate, $FeAsO_4$. The crystals are monoclinic with $a:b:c = 0·6155:1:0·3221$; $\beta = 77°8'$. Cleavage $c(001)$, perfect. D 4·32. Mean refractive index (Na), 1·78.
L. J. S.

Further Experiments on the Synthesis of Wulfenite. E. Dittler (*Zeitsch. Kryst. Min.*, 1914, **54**, 332—342. Compare A., 1913, ii, 1063).—Attempts to prepare wulfenite ($PbMoO_4$) by the action of a solution of lead hydrogen carbonate in water containing carbon dioxide on calcium molybdate, or by prolonged digestion of normal lead carbonate ($PbCO_3$) or lead sulphide (PbS) with a concentrated solution of an alkali molybdate, did not lead to the desired result. L. J. S.

Molecular Destruction of Kaolinite by Heat. A. M. Sokolov (*Ber. Tech. Inst. K. Nikolaus I*, 1913, **22**, 1—15; from *Zeitsch. Kryst. Min.*, 1915, **55**, 195—196).—Kaolinite from Gluchov was heated for periods of one to five hours at temperatures of 200—1000°, and the loss of water determined. The residue was digested for two hours with 16% hydrochloric acid, and the soluble alumina determined. The results obtained after ignition for one hour are:

Temp.	Loss of H_2O %.	Soluble Al_2O_3 %.	Molecular ratio $Al_2O_3 : H_2O$.
300°	0·72	2·12	1 : 1·91
400	0·67	2·08	1 : 2·03
600	10·49	28·46	1 : 2·14
700	11·92	32·30	1 : 2·06
800	12·99	34·66	1 : 2·12

With more prolonged heating, slightly higher results were obtained. From the residue a weak alkali solution extracts soluble silica. At 800° the kaolin molecule is completely broken down into its component oxides, and on this depends the method of Zemiatchensky for the analysis of clays. L. J. S.

Silicate Fusion Solutions. K. Neubauer (*Foldtani Közlöny*, 1911, **41**, 72—85, 197—205; from *Zeitsch. Kryst. Min.*, 1914, **54**, 184).—Experiments were conducted under the microscope with mixtures of leucite, orthoclase, and diopside in various proportions. Fusion began at 1190—1205°, that is, about the melting point of orthoclase (1190°), and was complete at a point near the arithmetical mean of the melting points of the three components. Crystallisation began at a temperature (1090—1170°) lower than the m. p. of any of the components. Crystals of leucite separated first, and then good crystals of diopside, which grow very rapidly. Orthoclase separated only as a glass. L. J. S.

Analyses of Venetian Minerals. E. Billows (*Zeitsch. Kryst. Min.*, 1916, **55**, 389—390; from separate publication, *Padua*, 1912).—Allophane (anal. I) is found in an old lead mine on Monte Civillina. It is earthy or forms compact masses, white or brown in the interior, with a glassy sky-blue exterior crust. Analcite (II), crystals from druses in the augite-porphyrite of the Val dei Zuccanti. Heulandite (III), as red scales in druses in altered augite-porphyrite from the same locality. *Arduinite* (IV), a new mineral, previously regarded as natrolite, from the Val dei Zuccanti. It forms red, radially fibrous aggregates. The fibres give straight extinction and are optically negative; they show traces of cleavage in the direction of their length. Analysis IV corresponds with the formula $(Na_2,Ca)AlSi_3O_8,2\frac{1}{2}H_2O$.

	SiO_2.	Al_2O_3.	Fe_2O_3+ Mn_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
I.	28·01	37·17	1·42	0·23	—	—	32·08	100·34*	1·94
II.	54·08	20·95	1·78	0·40	1·02	14·01	7·82	100·06	2·24
III.	57·96	15·78	2·04	8·10	0·21	2·16	14·67	100·92	2·17
IV.	49·40	14·57	2·43	6·57	1·54	11·77	13·85	100·13	2·26

* Including also: Cr_2O_3, trace; ZnO, 0·79; CuO, 0·64.

L. J. S.

Microchemical Examination of Ittnerite and Scolopsite. ST. J. THUGUTT (*Sitzungsber. Warschauer Ges. Wiss.*, 1911, 79—87; from *Zeitsch. Kryst. Min.*, 1914, **54**, 197).—Colour reactions (with methylene-blue, or 10% silver nitrate solution and 20% potassium chromate solution) indicate that these doubtful minerals are mixtures of haüyne, gismondite, calcite, and pyrrhotite (or an alkali sulphoferrite). The fact that gismondite has been derived from haüyne suggests that the radicles $CaAl_2Si_3O_{10}$ and $CaAl_2O_4$ enter into its constitution. L. J. S.

Zeolites from Neubauerberg, Leipa, Bohemia. R. GÖRGEY (*Mitt. naturwiss. Ver. Univ. Wien*, 1911, **9**, 17; from *Zeitsch. Kryst. Min.*, 1914, **54**, 409).—Fine specimens of zeolites are found at this locality. The species represented are natrolite, analcite, chabazite, apophyllite, gyrolite, mesolite, thomsonite, heulandite, and phillipsite. Thomsonite is the latest formed mineral in the amygdales, and forms white, compact, asbestos-like masses; analysis by B. Mauritz gave:

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	H_2O.	Total.	Sp. gr.
42·66	27·53	12·43	4·59	0·20	13·42	100·83	2.290

L. J. S.

Mineralogy of Graves Mountain, Georgia. T. L. WATSON and J. W. WATSON (*Bull. Phil. Soc. Univ. Virginia, Sci. Ser.*, 1912, **1**, 200—221; from *Zeitsch. Kryst. Min.*, 1916, **55**, 411).—Analyses are given of pyrophyllite (I), lazulite (II), and kyanite (III):

	SiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
I.	64·90	—	26·88	1·18	—	0·74	0·17	5·69	99·57	2·659
II.	6·05	38·25	33·92	—	3·99	3·12	9·08	5·83	100·24	2·958
III.	39·14	—	59·52	1·09	—	0·18	0·40	—	100·33	3·282

L. J. S.

Stilbite and Chabazite from Hungary. AL. VENDL (*Földtani Közlöny*, 1911, **41**, 70—71, 195—196; from *Zeitsch. Kryst. Min.*, 1914, **54**, 181—182).—Stilbite from Mt. Csódi, near Dunabogdány, gave I, and chabazite from Somosújfalu, comitat Nográd, gave II.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	56·21	16·01	trace	8·11	—	—	0·24	19·17	99·74
II.	49·81	18·42	trace	7·66	trace	0·10	1·22	22·32	99·53

L. J. S.

Microchemical Examination of Zeagonite. ST. J. THUGUTT (*Sitzungsber. Warschauer Gesell. Wiss.*, 1911; from *Zeitsch. Kryst. Min.*, 1914, **54**, 198).—Groth and Zambonini have regarded zeagonite as a basic and somewhat weathered phillipsite. Zeagonite from Vesuvius was found to contain 15·87% H_2O, that is, only slightly less than in normal phillipsite. In methylene iodide solution (1:1000 H_2O), the mineral shows a lilac colour by transmitted light and blue by reflected light. With 10% silver nitrate solution and potassium chromate it gives a faint orange coloration, which is more distinct at 100°. The reactions resemble those for phillipsite, but with slight differences. The mineral is regarded as a natural dehydration product of a phillipsite poor in silica. The zeagonite from Löbau is shown to be a mixture of phillipsite with 15—25% levynite. L. J. S.

Crystallised Montmorillonite and a Gel form of Planerite. HANS LEITMEIER (*Zeitsch. Kryst. Min.*, 1916, **55**, 353—371).—A yellow clay mineral from the Progress mine (copper, lead, and silver) in the Hermanli district, Zogora, Bulgaria, when received was a perfectly isotropic gel, but after being kept for three years it showed throughout the larger part a feeble birefringence, indicating that it had become crystalline. This is supposed to have been brought about by an increase in the size of the grain of the material. Analysis I agrees with the formula

$$Al_2Si_4O_{11},6H_2O.$$

	SiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	CuO.	CaO.	MgO.	Insol.	H_2O.	Total.
I.	50·14	—	19·74	4·14	—	1·26	2·28	—	22·61	100·17
II.	0·16	29·06	30·46	0·54	3·81	—	0·18	1·49	34·07	99·77
III.	0·21	28·84	31·00	0·92	—	trace	0·36	2·55	34·78	98·66

Planerite occurs as white and blue compact masses in the manganese ore deposits of Arschitza, near Jakubeny, in Bukovina. It is colloidal and optically isotropic ($n_{Na} = 1·5167$), $H < 2$. Analysis II of the blue material gives the formula $Al_6P_4O_{19},18H_2O$. The amount of water depends on the vapour pressure, and the loss proceeds continuously with rise in temperature; the formula is therefore written $Al_6P_4O_{19},nH_2O$. At 100°, with $10H_2O$, the mineral is identical chemically with the crystallised planerite. It belongs to the wavellite type with $Al_2O_3:P_2O_5 = 3:2$. Analysis III is of the white, less pure, material. This, when treated with a solution of copper ammonium sulphate, adsorbs 5·8% CuO. The copper in the blue mineral is therefore not an essential constituent, but adsorbed in the gel. Taking the copper into account, the formula for the blue mineral becomes $CuO,6Al_2O_3,4P_2O_5,40H_2O$, or at 100° with $20H_2O$. Cœruleolactite (T. Petersen, 1871) is identical with planerite (R. Hermann, 1862). L. J. S.

The Constitution of some Minerals of the Mica Group in the Light of the Stereo-Hexite-Pentite Theory. W. ASCH and D. ASCH (*Zeitsch. Kryst. Min.*, 1915, **54**, 584—586).—In accordance with his theory that orthosilicates can form isomorphous mixtures with polysilicates, for example, trisilicates, Clarke has been led to ascribe very complex formulæ to the alumino-silicates "zinnwaldite" and cryophyllite (A., 1890, 460). According to the present authors, the same analyses employed by Clarke lead, in accordance with the hexite–pentite theory, to much simpler formulæ. Thus "zinnwaldite" appears to be derived from the aluminosilicic acid, $nH_2O,2(5Al_2O_3,18SiO_2)$, by the replacement of part of the hydrogen by basic atoms and of part of the oxygen by fluorine. The composition of the mineral is expressed by the formula $K_{10}Li_{10}H_4Mn''Fe''_7Al_{20}Si_{36}F_{20}O_{112}$.

Cryophyllite is found to have the composition

$$H_3K_4Li_5Fe''_{1\cdot5}Al_{55}Fe'''_{0\cdot5}F_6Si_{15}O_{43\cdot5},$$

and can be regarded as a derivative of the aluminosilicic acid, $7\cdot5H_2O,3Al_2O_3,15SiO_2$. Structural formulæ are given for both minerals. E. H. R.

The Limestones and Calciphyres of Candoglia, Italy.

E. Tacconi (*Atti Soc. Ital. Sci. Nat.*, 1911, **50**, 55—93; from *Zeitsch. Kryst. Min.*, 1914, **54**, 388—389).—A detailed description of the rocks and minerals from this locality. A violet-blue mineral occurring with pistachio-green epidote in syenite-pegmatite is shown by the following analysis to belong to the epidote group. Its optical characters (high refractivity, feeble negative birefringence, 2V = 60—80°, dispersion, $v > \rho$) suggest a ferriferous clinozoisite.

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	H_2O.	Total.
41·60	20·11	14·23	trace	20·16	1·58	1·94	99·62

L. J. S.

Uralite from Uralite-porphyrite from Pellinge, Finland.

Eere Mäkinen (*Geol. För. Förh.*, 1915, **37**, 633—638; from *Jahrb. Min.*, 1917, i, 142—143).—Pseudo-crystals of uralite (anal. I, D 3·118) isolated from uralite–porphyrite (anal. II) from Sådholmen, Pellinge, show the short, prismatic form characteristic of volcanic augite and the optical constants of hornblende; the latter being in agreement with the data of Ford, which showed a correlation with the chemical composition (A., 1914, ii, 211).

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.
I.	49·58	0·28	6·82	3·35	12·35	—	14·00
II.	56·06	0·92	13·97	1·41	7·59	0·09	6·95

	CaO.	Na_2O.	K_2O.	H_2O+.	H_2O-.	Total.
I.	11·68	0·33	0·28	1·45	0·50	100·62*
II.	9·48	2·06	0·63	0·56		99·72

* Also F, about 0·2%.

L. J. S.

Petrography of the Central Caucasus.

K. J. Timoféev (*Ann. Géol. Min. Russie*, 1912, **14**, 170—173; from *Zeitsch. Kryst. Min.*, 1915, **55**, 203).—Porphyritic crystals of a rhombic pyroxene in andesite-dacite from the Keli plateau gave the following results, agreeing with the formula $FeSiO_3,3MgSiO_3$. The mineral may therefore be regarded either as a bronzite rich in iron or as a hypersthene poor in iron.

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Total.
54·07	3·20	5·12	12·73	3·58	21·24	99·94

L. J. S.

Rare Californian Minerals. A. F. Rogers (*School Mines Quart. New York*, 1912, **33**, 373—381; from *Zeitsch. Kryst. Min.*, 1916, **55**, 408).—Twenty-eight species are described. Analysis of crocidolite from Santa Clara County gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	H_2O.	Total
50·65	0·90	19·21	21·70	0·79	0·39	[4·93]	1·43	100·00

L. J. S.

Geometric Properties of Isomorphous Mixtures. Application to the Rhombic and Monoclinic Pyroxenes. A. Ledoux (*Bull. Soc. franç. Minéral.*, 1916, **39**, 232—280; from *Chem. Zentr.*, 1917, ii, 37).—The author develops the relationship between the geometric constants, the chemical composition, and the density of substances in general, and for isomorphous mixtures of several components from the theoretical and mathematical side, and applies the theory to the rhombic and monoclinic pyroxenes. From an examination of several of the latter, the values of the molecular axes of the following theoretical silicates are deduced: $MgSiO_3$, $FeSiO_3$, $CaSiO_3$, $CaMg(SiO_3)_2$, $CaFe(SiO_3)_2$, and $LiAl(SiO_3)_2$. The data at present available are insufficient for the silicates containing manganese and for those with sesquioxides, such as aegirine. In the series enstatite–hypersthene and diopside–hedenbergit, the molecular axes increase with the molecular weight, that is, with the iron content. The molecular axes of a chemical compound differ from those of an isomorphous mixture of similar composition. The alteration of the molecular axes of a pyroxene which is caused by the addition of a certain molecule is not constant, but depends greatly on the nature of the pyroxene. One and the same molecule can cause diametrically opposite alterations when introduced into two different pyroxenes. A number of changes caused by the introduction of certain molecules into the diopside–hedenbergite series are discussed in detail. H. W.

Synthetical Experiments in the Pyroxene Group. Vera Schumoff-Deleano (*Centr. Min.*, 1917, 290—304).—Experiments were made with a view to obtain a clue towards the constitution of aluminous augite. Diopside was fused with varying amounts (4·5—17%) of alumina, and the resulting material slowly crystallised. There were formed homogeneous crystals of a pyroxene containing in solid solution up to about 15% Al_2O_3, which is not extracted by digesting the material with alkali hydroxide solution.

In the presence of more alumina, felspar, sillimanite, or spinel separates out. A fusion with the composition $MgAl_2SiO_6$ (a molecule often assumed to enter into the composition of aluminous augite) is unstable, and yields magnesia-anorthite, or above 1400° spinel and glass. Experiments with diopside and ferric oxide gave similar results, about 15% Fe_2O_3 being taken up in solid solution. When, however, alumina and ferric oxide are both present, magnetite, olivine, and felspar are formed. Hexagonal calcium metasilicate (α-$CaSiO_3$) and enstatite are also capable of taking up about 15% Al_2O_3 in solid solution. L. J. S.

Artificial Iron-Rhodonite in Slags from Elba, Italy. E. TACCONI (*Rassegna Mineraria, Metallurgia e Chim.*, 1911, **34**, No. 9; from *Zeitsch. Kryst. Min.*, 1914, **54**, 392).—Bessemer slags from Porto Ferrajo yielded brown, tabular and prismatic crystals, which the following analysis proves to be an iron-rhodonite, $(Mn,Fe)SiO_3$, with an absence of calcium and magnesium. The crystallographic constants, $a:b:c=1·07285:1:0·62127$; $\alpha=103°18'$, $\beta=108°44'8''$, $\gamma=81°39'16''$, are near to those of natural rhodonite.

SiO_2.	MnO.	FeO.	Al_2O_3.	Total.
43·32	32·30	22·41	1·76	99·79

L. J. S.

Gadolinite from the Radauthal, Harz. J. FROMME (*Centr. Min.*, 1917, 305—307).—Crystals of gadolinite occur with quartz, prehnite, and orthite (A., 1910, ii, 314) in small cavities in graphic granite. D^{15} 4·298. Analysis gave:

SiO_2.	ThO_2.	Y_2O_3.	Ce_2O_3.	$(Nd, Pr, La)_2O_3$.	Fe_2O_3.	FeO.
23·86	2·26	35·86	6·33	5·49	1·13	11·75

MnO.	CaO.	MgO.	K_2O.	Na_2O.	GlO.	Ign.	Total.
0·14	1·54	0·11	0·38	0·65	8·75	1·20	99·45

Reckoning CaO, Na_2O, etc., with the iron, and the loss on ignition with the glucinum, these results agree with the usual formula $Fe''Gl_2Y_2Si_2O_{10}$. The material is perfectly fresh, but a portion at least of the loss on ignition consists of water. L. J. S.

The Volcanic Exhalation. ALBERT BRUN (*Arch. Sci. phys. nat.*, 1917, [iv], **44**, 5—18).—An examination of the salts and fumarole products from numerous eruptions of Vesuvius during one hundred years, from Spagnuolo, Etna, Chineyro, Vulcano, Pico de Teyde, and Kilauea, and of volcanic specimens from great depths in the Pacific, and of a large number of specimens of lava from different sources. In addition to the elements already recognised, boron, lithium, and thallium are found to be present in the paroxysmal volcanic exhalation. The occurrence of these elements in the eruptive magmas is fairly general. Soluble thallium chloride was found in the ammonium salts from Vesuvius and Chineyro and in certain halites from Vesuvius. An insoluble thallium compound was found penetrating the red and violet scoriæ, more or less altered by fumarole emanations. The sulphide of thallium and arsenic was found associated with the red crusts of realgar and orpiment from Vesuvius in 1906. The presence of thallium and lead is consdered to be a confirmation of the values for the mean density of the earth as found by astrophysicists. W. G.

The Hornblende-bearing Lavas of Etna. S. DI FRANCO (*Atti Accad. Gioenia, Catania*, 1911, [v], **4**, No. 3, 1—12; from *Zeitsch. Kryst. Min.*, 1914, **54**, 204).—Several of the lavas of Etna contain enclosures and crystals of hornblende. At Milo these crystals measure 2—4 cm. in the direction of the vertical axis. Analysis gave:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	Ign.	Total.	Sp. gr.
40·10	2·05	14·71	9·60	4·83	12·13	11·64	0·78	4·07	0·58	100·49	2·97

L. J. S.

The Brahin Meteorites. L. L. IVANOV (*Ann. Géol. Min. Russie*, 1912, **13**, 72—76; from *Zeitsch. Kryst. Min.*, 1915, **55**, 164).—A meteorite found near the village of Kruki, 33—35 versts west of Brahin, in govt. Minsk, Russia, shows the typical structure of a pallasite; and the following analysis of the metallic portion (D 7·49) agrees closely with that made by Inostranzev in 1869 of the Brahin mass. It is concluded that the Kruki, Krukov, and Kuzovka meteorites all belong to the Brahin fall.

Fe.	Ni.	Co.	Mg.	Ca.	SiO_2.	S.	Insol.	Total.
88·58	8·38	1·07	1·12	trace	0·47	n.d.	9·39	100·01

L. J. S.

Olivine from the Brahin Meteorite. K. J. TIMOFÉEV (*Ann. Géol. Min. Russie*, 1912, **14**, 169; from *Zeitsch. Kryst. Min.*, 1915, **55**, 202).—Analysis of the olivine from the meteorite found near the village of Kruki, govt. Minsk, Russia, gave:

SiO_2.	Al_2O_3.	FeO.	MgO.	MnO.	Total.
39·87	0·35	11·96	47·35	—	99·53

L. J. S.

Analytical Chemistry.

p-Nitrophenol as an Indicator in Water Analysis. A. GOLDBERG (*Chem. Zeit.*, 1917, **41**, 599).—Although methyl-orange and *p*-nitrophenol are equally sensitive as indicators in estimating the acidity of natural waters, the colour change of *p*-nitrophenol renders its use more suitable in the case of turbid waters. *p*-Nitrophenol is not altered by boiling with water under pressure.

W. P. S.

[Stable Starch Solution.] Pollitz (*Zeitsch. angew. Chem.*, 1917, **30**, i, 132).—The addition of a very small quantity of an alkali, for example, sodium hydroxide, prevents the bacterial decomposition of starch solution; the quantity of alkali necessary is too small to have any influence when the starch solution is used as an indicator in iodometric titrations. W. P. S.

A Substitute for Litmus for Use in Milk Cultures. Wm. Mansfield Clark and Herbert A. Lubs (*J. Agric. Research*, 1917, **10**, 105—111).—The authors recommend the use of dibromo-*o*-cresolsulphonephthalein (compare A., 1916, ii, 570) in place of litmus or azolitmin as an indicator for following the changes in hydrogen-ion concentration of milk cultures. The new indicator is preferable to litmus in that it does not undergo reduction during sterilisation in the presence of milk; it can be used in very high dilution (0·005% in the form of its sodium salt); it is of definite composition, being a crystalline compound; if other conditions are constant, it will always produce the same coloration for the same P_H of the milk. Comparative tests were made of the two indicators, using a variety of organisms, and it was found that any change in reaction which could be observed with litmus could be followed equally well with the new indicator. Some of the difficulty experienced in reproducing a particular initial colour with either indicator is shown to be due to the changes in P_H which occur when milk is sterilised by heat. W. G.

Fallacies in Colorimetry. William M. Dehn (*J. Amer. Chem. Soc.*, 1917, **39**, 1392—1398).—The author discusses the physical and chemical sources of error in colorimetry, illustrating his remarks by reference to Folin's creatinine estimation, and appending a long bibliography on the subject. J. C. W.

A Titration Flask. F. K. Bezzenberger (*J. Amer. Chem. Soc.*, 1917, **39**, 1321).—The flask is recommended as a substitute for the ordinary weight burette. It is a conical one fitted with a ground-glass stopper, through which passes a relatively wide tube reaching nearly to the bottom of the flask and with its upper end ground to fit the exit tube from the stock reagent bottle. The tube is also provided with a ground-glass cap. The flask communicates with the exterior through a capillary tube, which also passes through the ground-glass stopper and enables the wider tube to be rinsed by slightly increasing the pressure in the flask and allowing the solution thus raised to run back. H. M. D.

Filter Flask. Jos. A. Shaw (*J. Ind. Eng. Chem.*, 1917, **9**, 793).—The flask has the form of an ordinary pear-shaped separating funnel. A side-tube is provided near the top for connecting the flask with the pump. The tap at the bottom has a wide bore, whilst the tubulure at the top is of a size suitable for taking the rubber stopper holding the stem of the filter funnel. W. P. S.

Analysis of Very Small Quantities of Gas. L. Hamburger and W. Koopman (*Chem. Weekblad*, 1917, **14**, 742—752).—A description of a form of microgas-analysis apparatus adapted to the estimation of carbon dioxide and monoxide, hydrogen, methane, and nitrogen. A. J. W.

Granular Calcium Chloride as a Drying Agent. A. T. McPherson (*J. Amer. Chem. Soc.*, 1917, **39**, 1317—1319).—Experiments made with a view to test the efficiency of granular calcium chloride as a drying agent show that the substance which has been heated at 260—275° in a current of air dried over phosphoric oxide, may be used for the rapid removal of every weighable trace of moisture from a comparatively large volume of gas. The amount of air which can be dried efficiently decreases as the rate of passage of the air over the granular chloride increases. H. M. D.

Comparison of the Efficiency of some Common Desiccants. Mary V. Dover and J. W. Marden (*J. Amer. Chem. Soc.*, 1917, **39**, 1609—1614).—The method employed by Baxter and Starkweather (A., 1916, ii, 637) for the comparison of the efficiencies of various desiccating agents, has been applied in the investigation of aluminium oxide, magnesium oxide, and cupric sulphate.

The results obtained show that aluminium oxide is a very efficient drying agent, and that the temperature at which this substance has been previously heated does not appreciably affect its capacity for absorbing moisture. A table is given showing the quantities of water contained in 1 litre of air which has been passed through a 30 cm. column of various desiccating agents at 25°. This table shows that aluminium trioxide, (Al_2O_3,xH_2O), potassium hydroxide, and resublimed phosphoric oxide are the three most efficient drying agents. H. M. D.

New Method for the Estimation of Hydrogen Peroxide. George S. Jamieson (*Amer. J. Sci.*, 1917, [iv], **44**, 150—152).—The method is based on the addition of a measured volume of hydrogen peroxide solution to an alkaline solution containing an excess of standard sodium arsenite. After two minutes, concentrated hydrochloric acid is added to the solution, and the unchanged arsenite is titrated with a standard solution of potassium iodate in the presence of chloroform as indicator. H. M. D.

Iodometric Estimation of Chlorine in Chlorides. Gregory Torossian (*J. Ind. Eng. Chem.*, 1917, **9**, 751—752).—The chloride is mixed with finely powdered manganese dioxide and heated with the addition of sulphuric acid (1 : 1). The liberated chlorine is passed into potassium iodide solution, and the iodine which is set free is titrated with *N*/10-thiosulphate solution. The sulphuric acid used must be free from nitric acid, nitrous acid, and hydrochloric acid; fluorides, if present in the chloride, do not interfere, and their action on the glass vessels is not appreciable. W. P. S.

Volumetric Estimation of Chlorine in Foods, etc., without Formation of Ash by the Wet Method. A. Weitzel (*Arb. K. Gesundh. Amt.*, 1917, **50**, 397—404; from *Chem. Zentr.*, 1917, i, 973—974).—Small quantities of chlorine are readily lost in the customary estimation of this substance in the ash of organic substances. Two processes are therefore described which are available for foods, etc., and do not necessitate the preparation of an ash. According to the material, decomposition is effected with nitric acid or sodium hydroxide. The examination of meat or dog biscuit is effected as follows. Air-dried meat (2 grams) or biscuit (5 grams) is heated with nitric acid (D 1·15, 20 c.c. or 50 c.c.) under reflux on the boiling-water-bath, with occasional shaking, for thirty minutes. Water (50 c.c. or 20 c.c.) is now added, and the mixture is heated over gauze to gentle boiling for fifteen minutes. The cooled liquid is treated with 10 c.c. of silver nitrate solution (1 c.c. = 0·005 gram NaCl), warmed for fifteen minutes on the steam-bath, cooled, diluted with water to 100 c.c., and filtered. The excess of silver nitrate is estimated in 50 c.c. of the filtrate by titration with ammonium thiocyanate in the presence of iron alum.

In the examination of ling and salted fish roe, 2 to 5 grams of the powdered, sieved, air-dried substance (according to the chlorine content) are heated on the steam-bath with occasional shaking during thirty minutes with potassium hydroxide solution (10%, 20—50 c.c.); after being cooled, the solution is diluted to 250 c.c. Twenty-five c.c. of this solution are mixed with nitric acid (D 1·15, 20 c.c.) and standard silver nitrate (20 c.c.), and the mixture is heated under reflux to gentle ebullition until the colour becomes pale. The cold liquid is diluted to 100 c.c., filtered, and the chlorine estimated in 50 c.c. of the filtrate. The process yields accurate results, which are slightly higher than those obtained by the usual method, because, in the latter case, small amounts of alkali chlorides are lost by volatilisation. H. W.

Estimation of Chlorides in Body Fluids. Victor John Harding and Edward H. Mason (*J. Biol. Chem.*, 1917, **31**, 55—58).—A modification of McLean and Van Slyke's method (A., 1915, ii, 573), in which the proteins of the blood are removed by copper sulphate and sodium hydroxide instead of by Merck's blood charcoal. H. W. B.

Water Analysis. IV. L. W. Winkler (*Zeitsch. angew. Chem.*, 1917, **30**, i, 113—116. Compare A., 1916, ii, 448).—Methods are described for the detection and estimation of bromine, iodine, and arsenic in water and waste-waters. Bromine is estimated by distilling with sulphuric acid, potassium permanganate, and manganous sulphate after the bromine has been concentrated in a distillate by distilling the water with sulphuric acid, sodium chloride, and a definite quantity of permanganate. Iodine is found by decomposing the iodides with sulphuric acid and sodium nitrite, and the quantity of iodine is estimated iodometrically. For the detection of arsenic, a modification of the Gutzeit test is recommended, gold chloride being used on linen to obtain the stain. W. P. S.

Titration of Iodine with Thiosulphate. RICHARD KEMPF (*Zeitsch. angew. Chem.*, 1917, **30**, i, 71—72).—Attention is directed to the importance of avoiding the use of an excess of mineral acids in iodine solutions which have to be titrated with thiosulphate solution. This particularly applies to the titration of iodine liberated when ferric chloride solution is treated with potassium iodide. The added thiosulphate tends to be decomposed locally by the hydrochloric acid before it comes into contact with the iodine. W. P. S.

Estimation of Dissolved Oxygen in Water in the Presence of Nitrites and Organic Substances. H. NOLL (*Zeitsch. angew. Chem.*, 1917, **30**, i, 105—108).—Nitrites may be destroyed, previously to the estimation of dissolved oxygen, by treating the water with 1 c.c. of 50% carbamide solution and 1 c.c. of 25% sulphuric acid, and allowing the action to proceed for four hours; the use of 10% carbamide solution, as recommended by Lehmann and Fitzau, gives high results for the oxygen. Clarke's method (A., 1911, ii, 928) is untrustworthy, whilst Winkler's method (A., 1915, ii, 277) yields accurate results, particularly when sodium hydrogen carbonate is used to convert the manganous hydroxide into manganous carbonate. Rideal and Stewart's (A., 1901, ii, 472) method is also trustworthy. W. P. S.

Estimation of Ozone and Oxides of Nitrogen in the Atmosphere. FRANCIS LAWRY USHER and BASUR SANJIVA RAO (T., 1917, **111**, 799—809).—After a criticism of the various methods available for the estimation of ozone, nitrogen peroxide, and hydrogen peroxide in small quantities, the authors describe a method for the estimation of these substances in the air. The principle consists in the action of a standard solution of sodium nitrite in faintly alkaline solution on the gas under examination. In this way, nitrate is produced by the ozone, nitrate and nitrite by the nitrogen peroxide, and hydrogen peroxide has no action. For details as to the procedure, the original paper should be consulted. The method is sensitive to 1 part of nitrogen peroxide in 56 millions of air. J. F. S.

Estimation of Hydrogen Sulphide in Water at the Place where the Sample is Collected. G. INCZE (*Zeitsch. anal. Chem.*, 1917, **56**, 308—310).—The water is collected in a 300 c.c. flask and 3 c.c. of silver nitrate–ammonium nitrate solution (85 grams of silver nitrate and 200 grams of ammonium nitrate per 500 c.c.) are added. The contents of the flask are shaken, the precipitate then allowed to settle, and 101 c.c. of the clear liquid are drawn off, and the excess of silver is titrated with $N/50$-thiocyanate solution. In this titration, sulphide and chloride are estimated together. Another portion of the water is boiled to expel hydrogen sulphide, and the chloride is then titrated. The difference between the two titrations is multiplied by 0·0034 to give hydrogen sulphide in mg. per litre of water. W. P. S.

Use of Hydrazine Sulphate and Potassium Bromide in the Estimation of Sulphides in Ores. H. SCHEIDLER (*Chem. Zeit.*, 1917, **41**, 580).—A mixture of hydrazine sulphate and potassium bromide is an efficient substitute for stannous chloride for preventing the decomposition of hydrogen sulphide by ferric chloride. Five grams of potassium bromide and 3 grams of hydrazine sulphate are sufficient for 1 gram of roasted ore.

W. P. S.

Volumetric Estimation of Polysulphide, Monosulphide, and Thiosulphate Sulphur in Lime-Sulphur Liquids. A. WÖBER (*Chem. Zeit.*, 1917, **41**, 569—570).—The liquor is treated with an excess of mercuric chloride solution, ammonium chloride is added, and the mixture is titrated with *N*/10-sodium hydroxide solution; each c.c. of this solution is equivalent to 0·003206 gram of thiosulphate sulphur, $2CaS_2O_3 + 3HgCl_2 + 2H_2O = 2CaSO_4 + 4HCl + (2HgS{\cdot}HgCl_2)$. Another portion of the sample is heated with an excess of *N*-sodium hydroxide solution and hydrogen peroxide, and the excess of alkali is then titrated: $CaS_4 + 6NaOH + 13H_2O_2 = CaSO_4 + 3Na_2SO_4 + 16H_2O$; $CaS_5 + 8NaOH + 16H_2O_2 = CaSO_4 + 4Na_2SO_4 + 20H_2O$; $CaS_2O_3 + 2NaOH + 4H_2O_2 = CaSO_4 + Na_2SO_4 + 5H_2O$. Allowance is made for the thiosulphate in calculating the quantity of polysulphide sulphur. A further portion of the sample is then treated with an excess of *N*/10-iodine solution containing hydrochloric acid, and the excess is titrated with thiosulphate solution: $CaS_5 + I_2 = CaI_2 + 5S$; $CaS_2O_3 + I_2 = CaI_2 + CaS_4O_6$. This gives the quantity of monosulphide sulphur after allowance has been made for the thiosulphate. W. P. S.

Rapid Estimation of the Strength of Sulphuric Acid. H. DROOP RICHMOND and J. E. MERREYWETHER (*Analyst*, 1917, **42**, 273—274).—The method depends on the heat developed when sulphuric acid is diluted. Four hundred grams of water at about 18° are placed in a vacuum-jacketed flask provided with a stirrer and a thermometer reading to 0·01°. The temperature soon becomes constant and is noted; 5 c.c. of the sample are then added from a pipette, the latter is allowed to drain for fifteen seconds, and the mixture is stirred until the temperature is constant. The water equivalent of the calorimeter used by the authors was 14·5 grams, and the volume of sulphuric acid delivered by the 5 c.c. pipette averaged 4·911 c.c.; from these data, and from the results recorded by Pickering (T., 1890, **57**, 64), the following formula was calculated: $\% = 100 - 7{\cdot}6(3{\cdot}994 - R)$. The results obtained agree, within 0·1%, with those found by the ordinary volumetric method. W. P. S.

Chemical Control of Ammonia Oxidation. PAUL J. FOX (*J. Ind. Eng. Chem.*, 1917, **9**, 737—743).—For the examination of the gases used and produced in the oxidation of ammonia by passing it over a heated catalyst, it is recommended that the ammonia in the mixture of ammonia and air be estimated by direct absorption in standard acid. The exit gases from the plant contain nitric oxide, water vapour, oxygen, ammonium nitrate or nitrite, and nitrogen. The gas is first mixed with an excess of oxygen, then passed through an absorption vessel containing standard alkali solution, and next through a similar vessel containing alkali solution and hydrogen peroxide. Subsequent titration of the contents of the latter vessel, using sodium alizarinsulphonate as indicator, gives the quantity of nitric oxide present. The quantity of ammonia in the gases is found by treating the neutralised contents of the second absorption vessel with sodium hypobromite and measuring the volume of the evolved nitrogen. The nitrous acid is obtained by adding a measured volume of hydrogen peroxide to the contents of the first absorption vessel and titrating the mixture with permanganate solution; the hydrogen peroxide is also titrated separately with the permanganate solution, and the quantity of nitrous acid is calculated from the difference between the two titrations. W. P. S.

Estimation of Nitrogen in Nitrates and Nitrites. Th. Arnd (*Zeitsch. angew. Chem.*, 1917, **30**, i, 169—172).—Two hundred and fifty c.c. of the solution, containing about 0·05 gram of nitrogen (as nitrate or nitrite), are placed in a distillation flask and 5 c.c. of 20% magnesium chloride solution and 3 grams of finely divided copper–magnesium alloy (60% copper, 40% magnesium) are added. The mixture is distilled at once, 200 c.c. of distillate being collected in a receiver containing an excess of standard acid, and the excess is titrated in the usual way. If it is desired to work on a quantity of nitrate or nitrite equivalent to 0·1 gram of nitrogen, the amount of alloy used should be increased to 5 grams. W. P. S.

Estimation of Nitrate in Sewage by means of *o*-Tolidine. Earle B. Phelps and H. L. Shoub (*J. Ind. Eng. Chem.*, 1917, **9**, 767—770).—Twenty-five c.c. of the sample are boiled for thirty seconds with 0·5 c.c. of a solution containing 5% of sodium hydroxide and 1·5% of sodium chloride, then cooled, and 1 c.c. of the clear, supernatant liquid is evaporated in a porcelain basin. To the dry residue is added 0·2 c.c. of tolidine reagent (0·4 gram of *o*-tolidine in 100 c.c. of *N*/1-hydrochloric acid) and 0·5 c.c. of concentrated sulphuric acid, run gently down the sides of the dish, but not mixed. After five minutes, the liquid is caused to run round the side of the basin, 5 c.c. of water are added, the solution is transferred to a tube, diluted to 10 c.c., and the coloration compared at once with those obtained with definite quantities of standard nitrate solution. W. P. S.

The Forerunners of Kjeldahl's Method for Estimating Nitrogen. E. Salkowski (*Biochem. Zeitsch.*, 1917, **82**, 60—67).—Reference is made to a method of Heintz and Ragsky described in Hoppe-Seyler's "Handbuch der physiologisch- und pathologisch-chemischen Analyse" (1875) for the estimation of urea by conversion into ammonia by sulphuric acid. Also to a paper by Grete (*Ber.*, 1878, **11**, 1598). S. B. S.

Estimation of Nitrogen in Nitro-compounds. A. P. Sachs (*J. Soc. Chem. Ind.*, 1917, **36**, 915—916).—The somewhat low results obtained by Colver and Prideaux (this vol., ii, 340) in estimating nitrotoluenes by the stannous chloride reduction method are due to incomplete reduction of the nitro-compound under the experimental conditions. With the primary object of examining nitrated solvent naphthas, the author has modified the procedure in the following manner. The sample (0·2 gram) is heated in a sealed tube at 120° for two hours with 15 c.c. of stannous chloride solution ($SnCl_2,2H_2O$, 350 grams; 25% hydrochloric acid, 700 grams). The tube should be shaken every fifteen minutes, since otherwise dark particles due to carbonisation or tarry matters are sometimes formed. After being cooled, the contents of the tube are diluted with water to 100 c.c.; portions of 10 c.c. each are titrated with *N*/10-iodine, starch being used as indicator. A blank experiment should be performed simultaneously.

The method gives excellent results with nitrobenzene, *m*-dinitrobenzene, mononitrocymene, and with certain of the nitrated 'solvent naphthas,' but the problem cannot be considered as definitely solved. When time permits, the Dumas method is found to give the more trustworthy results. H. W.

Estimation of Phosphoric Acid in Phosphate Rock. C. C. Semple (*Eng. and Min. J.*, 1917, **103**, 1140—1141; from *J. Soc. Chem. Ind.*, 1917, **36**, 933).—The sample (0·5—1 gram) is decomposed by means of nitric and hydrochloric acids, and the silica is removed by twice evaporating to dryness in the customary manner. The dry residue is treated with hydrochloric acid (10 c.c.) and, after dilution with boiling water, the solution is filtered from insoluble matter and the latter is washed until the bulk of the filtrate and washings measures 175—200 c.c. Ammonia is added with constant stirring to this filtrate until a gelatinous precipitate of calcium, iron, and aluminium phosphates commences to form; ammonia (D 0·9, 30 c.c.) is then added in excess and the whole stirred vigorously. A saturated solution of citric acid (10 c.c.) is now added, and the solution is stirred for two minutes, at the end of which time, if the precipitated phosphates have not re-dissolved, more citric acid solution is added drop by drop until the phosphate solution is clear. Magnesia mixture (30 c.c.) is now added, and the solution is stirred until the precipitate of magnesium ammonium phosphate begins to be formed; after remaining for three hours it is filtered. The volume of citric acid required to clear the solution is proportional to the amount of phosphoric acid present in the liquid and, by use of a solution of citric acid of known strength for this purpose, an approximate idea of the strength of the sample may be obtained. The results agree closely with those obtained by the molybdate method. H. W.

Volumetric Estimation of Pyrophosphoric Acid. D. Balareff (*Zeitsch. anorg. Chem.*, 1917, **99**, 184—186).—A solution of sodium pyrophosphate, acidified with a known quantity of sulphuric or hydrochloric acid, may be titrated with sodium hydroxide, the maximum redness of phenolphthalein being taken as the end-point. The indication is sharper in presence of sodium chloride.

Sodium pyrophosphate solution may also be estimated by adding it to an excess of silver nitrate solution, collecting and washing the precipitate of silver pyrophosphate, and titrating the filtrate with thiocyanate. The silver cannot be replaced by lead.

Formulæ are given for the titration of ortho-, pyro-, and meta-phosphoric acids in the same solution with sodium hydroxide, the indicators used being methyl-orange, phenolphthalein, and silver nitrate–lacmoid (compare this vol., ii, 101). C. H. D.

Applications of Gas Analysis. I. Estimation of Carbon Dioxide in Alveolar Air and Blood, and the Carbon Dioxide Combining Power of Plasma, and of Whole Blood. Yandell Henderson and W. H. Morriss (*J. Biol. Chem.*, 1917, **31**, 217—227).—Simple apparatus is described for carrying out the above measurements with tolerable accuracy sufficient for clinical use. H. W. B.

Titration of Carbonic Acid and its Salts. I. M. Kolthoff (*Chem. Weekblad*, 1917, **14**, 780—793; *Zeitsch. anorg. Chem.*, 1917, **100**, 143—158).—Carbon dioxide in potable water can be estimated by titrating 100 c.c. with *N*/10-alkali hydroxide and 2 drops of 1% phenolphthalein as indicator. The reaction is complete when the rose-red colour persists for five minutes.

Alkali carbonates can be accurately titrated to alkali hydrogen carbonate by adding 10 c.c. of neutral glycerol to 25 c.c. of the liquid, and 1 drop of phenolphthalein as indicator. Standard acid is then slowly added until the colour is discharged. A. J. W.

Estimation of Carbonates in Limestone and other Materials. J. F. Barker (*J. Ind. Eng. Chem.*, 1917 **9**, 786—787).—An instrument similar to a hydrometer is used. The bulb of the instrument is divided into two parts: in the upper, concentrated hydrochloric acid is placed, whilst the limestone or other carbonate is placed in the lower part and water is added through the hollow, graduated stem until the latter, when placed in a cylinder of water, is immersed up to the zero mark. A tap connecting the two compartments of the bulb is now turned so as to admit the hydrochloric acid into the limestone chamber. As the carbon dioxide escapes through the hollow stem, the instrument rises in the water, and, when the reaction is complete, the graduation mark at the surface of the water is noted. This mark indicates the calcium carbonate content of the limestone. The stem of the instrument may be graduated so as to show directly either the calcium carbonate or carbon dioxide content of a sample. W. P. S.

Cobaltinitrite Method for the Estimation of Potassium. R. C. Haff and E. H. Schwartz (*J. Ind. Eng. Chem.*, 1917, **9**, 785—786).—The following procedure is recommended for the estimation of potassium in clinker, etc. Two grams of the sample are ground with 0·5 gram of ammonium chloride, the mixture is transferred to a platinum crucible containing a layer of calcium carbonate, another layer of calcium carbonate is placed over the mixture, and the mixture is heated strongly. After cooling, the mass is treated with water, the solution filtered, and the filtrate evaporated with the addition of an excess of acetic acid. The residue is dissolved in a small quantity of hot water, 15 c.c. of cobalt reagent (220 grams of sodium nitrite, 113 grams of cobalt acetate, and 100 c.c. of glacial acetic acid per litre) are added, and the mixture is evaporated to a pasty consistence. When cold, the precipitate is treated with 30 c.c. of cold water, collected on an asbestos filter, and washed once with cold water. The precipitate is then washed into a beaker containing an excess of *N*/5-potassium permanganate solution, the mixture is diluted to 250 c.c., heated for fifteen minutes on a water-bath, then acidified with 10 c.c. of sulphuric acid (1 : 1), a slight excess of *N*/5-oxalic acid solution is added, and, when the solution has cleared, this excess is titrated with *N*/5-permanganate solution. The amount of potassium present is calculated from the actual quantity of permanganate used. W. P. S.

Method of Ashing Organic Materials for the Estimation of Potassium. P. L. Blumenthal, A. M. Peter, D. J. Healy, and E. J. Gott (*J. Ind. Eng. Chem.*, 1917, **9**, 753—756).—To prevent loss of potassium salts by volatilisation during incineration, the organic substance should be treated with sulphuric acid in quantity more than sufficient to just moisten the sample, and the acid mixture then burnt to a white ash. The substance may also be evaporated with the addition of sulphuric acid and nitric acid before it is ignited. To estimate the potassium in the sulphated ash, the latter is dissolved in a few c.c. of dilute hydrochloric acid, the solution filtered, and the filtrate evaporated with platinum chloride. The precipitate is collected, washed with alcohol containing 10% of concentrated hydrochloric acid, then with 80% alcohol, and next treated with 6 c.c. of 20% ammonium chloride solution saturated previously with potassium platinichloride. The precipitate is now collected on an asbestos filter, washed with 80% alcohol, dried, and weighed. After the precipitate has been dissolved from the filter with hot water, the filter is dried and re-weighed. The difference between the two weights gives the quantity of potassium platinichloride obtained. W. P. S.

Methods of Titrating Mixtures of Hydrogen Carbonate and Carbonate or of Alkali Carbonate and Hydroxide necessitating neither Weighing nor previously Titrated Solutions. J. Clarens (*Bull. Soc. chim.*, 1917, [iv], **21**, 120—124). —The estimations are carried out by means of the ureometer previously described (compare A., 1909, ii, 826). A suitable amount of the mixture of carbonate and hydrogen carbonate is introduced into the flask and covered with water, 1 drop of methyl-orange being added as indicator. The whole is heated in a water-bath, and when equilibrium is reached the apparatus is closed and the acid is run in from the burette until the liquid is just neutral. The volume of acid V_m is read off and the level on the manometer. A similar experiment is performed, using a solution of pure normal carbonate, in quantity such that the reading on the manometer is approximately the same as in the first case. From the volume of acid used, v_n, the volume of acid, V_n, which with the requisite amount of carbonate would have given the original reading on the manometer, is calculated. Then the percentage of metal in the mixture existing in the form of hydrogen carbonate is given by $100(V_n - V_m)/V_m$. Similarly, if a mixture of carbonate and hydroxide is being examined, the percentage of hydroxide is given by $100(V_m - V_n)/V_m$. W. G.

A New Microchemical Reaction for Calcite. St. J. Thugutt (*Zeitsch. Kryst. Min.*, 1914, **54**, 197; from *Sitzungsber. Warschauer Ges. Wiss.*, 1911, 38—41).—Calcite intermixed with zeolites can be recognised by the following reaction. The powdered mineral (size of grains about 0·1 mm. diam.) is heated on platinum foil over a Teclu burner for fifteen seconds, and then treated with N/10-cobalt nitrate. The calcite becomes coated with a thin skin of a blue basic cobalt salt, whilst the zeolites are unaffected. Removing excess of the cobalt solution and adding N/10-silver nitrate, the bases of the zeolites are soon replaced by silver (detected with potassium chromate), whilst the basic cobalt salt becomes black owing to the formation of $Co(OH)_3$, and this quickly reduces the silver salt, producing a deposit of metallic silver on the calcite. L. J. S.

Calcined Magnesia. A. Astruc (*J. Pharm. Chim.*, 1917, [vii], **16**, 65—77, 110—115).—A discussion of the methods of examination and conditions as to purity given in the French Codex for calcined magnesia. As a result of the examination of a large number of samples of this substance, the author finds that none of the samples analysed conform to the Codex, and suggests new limits of variation which would not interfere with the medicinal value of the drug. In view of the difficulties in estimating small amounts of calcium in the presence of an excess of magnesium, the author proposes a rapid "diaphanometric" method. The sample under examination is dissolved in 10% acetic acid, using 0·1 gram in 25 c.c. of acid, and to it are added 5 c.c. of a 6% solution of oxalic acid. The precipitate thus obtained is compared against that obtained from a similar solution from a pure magnesia to which varying quantities of a standard calcium hydroxide solution have been added, careful note being made of the rate of appearance of the opalescence and the amount of precipitate formed. W. G.

Estimation of Zinc by Schaffner's Method. V. HASSREIDTER (*Zeitsch. anal. Chem.*, 1917, **56**, 311—316).—A discussion regarding the various modifications of this method. The average results obtained are trustworthy. W. P. S.

Volumetric Estimation of Zinc. J. W. SPRINGER (*Zeitsch. angew. Chem.*, 1917, **30**, i, 173—174).—Zinc may be titrated with ferrocyanide solution in the presence of iron and manganese if the solution containing the three metals is first boiled with the addition of bromine, then rendered ammoniacal, and titrated, while hot, with potassium ferrocyanide solution which has been standardised against pure zinc under similar conditions. Ferrous chloride solution containing acetic acid is used as an external indicator. The presence of manganese and ferric hydroxides does not interfere with the zinc–ferrocyanide reaction. W. P. S.

Electroanalysis of Zinc and Cadmium without Platinum Electrodes. J. GUZMÁN CARRANCIO and P. POCH (*Anal. Fis. Quim.*, 1917, **15**, 235—248).—An account of the estimation and separation of zinc and cadmium in acid solution and alkaline solution by Guzmán Carrancio's electrolytic method with a copper cathode and an anode of passive iron. A. J. W.

The Second Group in Qualitative Analysis. P. BRÄUER (*Zeitsch. J. physik. chem. Unterr.*, 1917, **30**, 36; from *Chem. Zentr.*, 1917, i, 1032).—A drop of a solution of mercuric sulphide in aqua regia is rubbed on aluminium foil by means of a piece of filter paper; a moderately thick layer of aluminium oxide, formed through the aluminium amalgam, is produced in a short time. H. W.

Estimation of Mercury in Galenical Preparations. HUGO WASTENSON (*Pharm. Post.*, 1917, **50**, 125—126; from *Chem. Zentr.*, 1917, i, 912—913).—The author applies in the present instance the method of destroying organic matter previously employed in analysing protein preparations containing silver (A., 1916, ii, 577). The substance (0·3—0·5 gram) is heated with concentrated sulphuric acid (10 c.c.) and nitric acid (D 1·4, 3 c.c.) until reddish-yellow vapours are not further evolved, the liquid has become clear and colourless, and the flask filled with sulphuric acid fumes. If the vapours still smell of sulphur dioxide, treatment with nitric acid (3 c.c.) is repeated. After being cooled, water (25 c.c.) is added, which is removed by evaporation. The cold solution is treated with water (15 c.c.) and potassium permanganate solution until a permanent pink coloration is produced; the latter is discharged with ferrous sulphate, the solution diluted with water (75 c.c.), and titrated with $N/10$-ammonium thiocyanate solution in the presence of ferric alum. The method is suitable for organic and inorganic preparations of the oxides of mercury, but not for such as contain the haloids. It can also be used for estimating mercury in ointments, plasters, and pills, provided that the ointments are tolerably free from paraffins.

H. W.

Volumetric Estimation of Mercuric Oxycyanide. ACHILLE TAGLIAVINI (*Boll. chim. farm.*, 1917, **56**, 297—299).—Mercuric oxycyanide, used by surgeons as a disinfectant, particularly for the hands, may be analysed as follows. A weighed quantity of 0·3—0·4 gram of the salt is dissolved in 50 c.c. of cold water, and the liquid, after treatment with 1 gram of sodium chloride and a drop of 0·2% methyl-orange solution, titrated with $N/10$-hydrochloric acid until it turns red. After the volume of acid required is read, 2 grams of potassium iodide are added to the solution, and the yellow liquid thus obtained is again titrated with $N/10$-hydrochloric acid as before. From the two volumes of acid required, the percentages of oxycyanide and cyanide in the salt may be calculated, the reactions proceeding according to the equations: (1) $HgO,Hg(CN)_2 + 2HCl = HgCl_2 + Hg(CN)_2 + H_2O$, and (2) $Hg(CN)_2 + 4KI + 2HCl = HgK_2I_4 + 2KCl + 2HCN$. T. H. P.

The Analysis of some Aluminium Alloys. J. H. STANSBIE (*J. Soc. Chem. Ind.*, 1917, **36**, 802—803).—For the estimation of silicon, copper, and manganese, the alloy (1 gram) is dissolved in a mixture of nitric acid and sulphuric acid, hydrochloric acid being afterwards added and the whole evaporated to fuming. All the soluble matter is taken up with water and the insoluble matter collected. After ignition and weighing, the insoluble residue is heated with hydrofluoric acid, and from the loss in weight the percentage of silicon calculated. In the filtrate from the insoluble matter the copper is estimated electrolytically, and then the manganese by the bismuthate method.

In order to estimate the zinc, 2 grams of the alloy are dissolved in 10% sodium hydroxide solution, and, after filtering through a pulp filter, the zinc is deposited on a copper-coated rotating cathode. The residue on the filter is dissolved in nitric acid and the copper estimated electrolytically, thus giving a check on the first method. If lead is present, it will show as peroxide on the anode, from which it is dissolved and estimated as sulphate. If more than 1% of iron is present, the filter pulp will be dark coloured, and should be heated with hydrochloric acid and washed. In the solution from which the copper and lead have been removed, the iron and traces of aluminium are precipitated as basic acetates, the iron and aluminium then being separated in the usual way. The final filtrate contains manganese and magnesium; the manganese is removed either as the sulphide or by means of bromine and ammonia, and the magnesium then precipitated and estimated as phosphate.

An alloy containing tin can be treated directly in the usual way with nitric acid, and the tin separated as oxide.

For the estimation of nickel (method due to F. G. BELTON), 1 gram of the alloy is dissolved in 25 c.c. of 20% sodium hydroxide solution. After dilution, the solution is filtered through a pulp filter and the residue washed with hot water and then with nitric acid (5 c.c. in 7 c.c. water). To the filtrate are added 3 c.c. of concentrated sulphuric acid, and the copper is estimated electrolytically. The solution is then diluted to 150 c.c., 10 grams of tartaric acid and 3 grams of ammonium chloride (to keep the aluminium in solution) are added, then ammonia in slight excess, and the nickel precipitated and estimated in the usual way with dimethylglyoxime. T. S. P.

Reaction of Manganese Salts. V. MACRI (*Boll. chim. farm.*, 1917, **56**, 377).—When a solution containing manganese, even in very small proportion, is rendered slightly alkaline and shaken and treated successively with a few drops of alkali oxalate solution and of acetic acid, the liquid assumes a distinct and persistent rose-red colour. The reaction is rendered more sensitive if the alkaline solution is boiled and then allowed to cool before the addition of oxalate and acetic acid, and also if one or two drops of hydrogen peroxide solution are added before the liquid is made alkaline. Salts of other metals do not interfere with the reaction, although those giving coloured solutions, especially if present in marked proportion, may mask it. T. H. P.

Rapid Estimation of Manganese and Chromium in Metallurgical Products. TRAVERS (*Compt. rend.*, 1917, **165**, 187—189).—A modification of Smith's method for the estimation of manganese by oxidation with ammonium persulphate in the presence of silver nitrate (compare A., 1905, ii, 66). For the estimation of manganese in steel, 0·2 gram of the steel is dissolved in 20 c.c. of nitric acid (D 1·1), the solution being poured into 30 c.c. of water. This solution is heated to 40—50° and 5 c.c. of *N*/10-silver nitrate and 1·5 c.c. of a saturated solution of ammonium persulphate are added. After three minutes the whole is poured into 100 c.c. of cold water and titrated with standard arsenious acid (0·65 gram of arsenious oxide per litre). This method is exact for manganese in the presence of chromium if the latter does not exceed 5—6% or if the manganese content is less than 0·15%.

For the estimation of chromium in chrome steels a similar oxidation is performed, the silver nitrate being unnecessary; a slight excess of standard arsenious acid is added, and the excess is titrated back with standard potassium permanganate. This method is applicable for chromium even in the presence of vanadium. W. G.

Analysis of Ferrum Hydrogenio Reductum. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1917, **30**, i, 64).—The quantity of metallic iron in this substance may be estimated approximately (within 0·5%) by simple ignition in contact with air. The increase in weight is due to the oxidation of the iron; 100 parts by weight of Fe give 142·9 parts of Fe_2O_3. W. P. S.

Separation of Nickel and Copper by means of Dimethylglyoxime. H. GROSSMANN and J. MANNHEIM (*Zeitsch. angew. Chem.*, 1917, **30**, i, 159—160).—The solution containing nickel and copper is treated with potassium sodium tartrate in quantity sufficient to keep the copper in solution when the mixture is rendered alkaline, and the nickel is precipitated by the addition of 1% alcoholic dimethylglyoxime solution and ammonia. The precipitate is collected, dissolved in hot dilute hydrochloric acid, and the nickel reprecipitated by the addition of potassium sodium tartrate, dimethylglyoxime, and a slight excess of ammonia. The copper is then precipitated as sulphide from the filtrates. W. P. S.

Apparatus for Electrometric Titration Depending on the Change of Oxidation Potential, and its Application to the Estimation of Small Quantities of Chromium in Steel. G. L. KELLEY, J. R. ADAMS, and J. A. WILEY (*J. Ind. Eng. Chem.*, 1917, **9**, 780—782).—A convenient combination of apparatus is described; it consists of a potentiometer system, motor for operating the stirrer, and burettes for the oxidising and reducing solutions. The estimation of chromium depends on the titration of chromates with ferrous sulphate, the electrometric apparatus being used for the measurements. W. P. S.

Estimation of Nitrotoluenes. E. DE W. S. COLVER and E. B. R. PRIDEAUX (*J. Soc. Chem. Ind.*, 1917, **36**, 856).—A reply to Knecht's comments on a previous paper by the authors (this vol., ii, 340). T. S. P.

Microanalysis of Wine. II. Estimation of Alcohol. MAXIMILIAN RIPPER and FRANZ WOHACK (*Zeitsch. landw. Versuchs-Wesen Österr.*, 1917, **20**, 102—114; from *Chem. Zentr.*, 1917, ii, 83—84. Compare this vol., ii, 106).—The process is an adaptation of Zeisel's iodide method. The original must be consulted for an exact description of the apparatus and necessary manipulation. The agreement of micro-analyses among themselves and with macrochemical estimations is generally very close. The maximum mean divergence from the average amounted in forty-seven cases to 0·15% with the former and 0·11% with the latter method. Identical results are obtained when 0·05 c.c. of wine (diluted to 0·5 c.c.) is used and when 100 c.c. are employed in the macrochemical analysis. The process is adapted to wine, beer, cider, brandy, etc. Wines containing up to 12% by volume of alcohol can be immediately investigated after dilution to ten times their volume; wines richer in alcohol require greater attention and are best diluted to twenty times their volume. The liberated iodine is titrated with $N/100$-thiosulphate solution in the presence of starch. The precautions necessary in using such dilute solutions are described. H. W.

Detection of Small Quantities of Glycerol. HANS WOLFF (*Chem. Zeit.*, 1917, **41**, 608—609).—Denigès's reaction for glycerol (conversion into dihydroxyacetone) is trustworthy for the identification of this substance, but it fails to distinguish glycerol from ethylene glycol, which is now used as a substitute for glycerol. Ethylene glycol, especially the commercial product, also yields aldehydic substances similar to acraldehyde when heated with potassium hydrogen sulphate. The refractometer, however, will differentiate glycerol from ethylene glycol; the refractometer number of ethylene glycol is less than 15, and of glycerol more than 55. W. P. S.

Estimation of Phenol in Commercial Cresylic Acid. J. J. Fox and M. F. Barker (*J. Soc. Chem. Ind.*, 1917, **36**, 842—845).—Previous methods for the estimation of phenol in tar acids (compare Masse and Leroux, A., 1916, ii, 650) have assumed that all the phenol is collected in the fraction of the tar acids distilling up to about 200°, and that the distillate at various temperatures is of constant composition. The authors' experiments show that this is by no means the case, and they have worked out a method which depends on the fact that the addition of a suitable proportion of *o*-cresol furnishes a mixture from which the whole of the phenol can be recovered in the first fractions of the distillate. The proportion of *o*-cresol to be added in an estimation is ascertained by a preliminary fractional distillation of the tar acids which have been separated from the crude cresylic acid. The volume of the cresylic acid distilling between 195° and 202° is noted, an equal volume of *o*-cresol is added to the original tar acids, and fractionation again carried out, the fraction up to 195° being collected and weighed. The freezing point of this fraction is now taken, after the addition of sufficient phenol to an aliquot portion to yield a mixture containing at least 80% of phenol. By means of the tables given by the authors, the percentage of phenol in the original sample can then be calculated.

The tables given are: Specific gravities at 15·5° of various mixtures of phenol with *o*-, *m*-, and *p*-cresol respectively; specific gravities at 15·5° of mixtures of *m*- and *o*-cresol, and of varying mixtures of phenol with *o*- and *m*-cresol and with *p*- and *m*-cresol. Boiling points of various mixtures of phenol with *o*-, *m*-, and *p*-cresol respectively, of mixtures of *o*- and *m*-cresol, and of phenol with various mixtures of *o*-, *m*-, and *p*-cresol. A table of the fractions obtained on the distillation of various mixtures of phenol and the three cresols. T. S. P.

Detection of Phenols by the Spectroscope. J. Formánek and J. Knop (*Zeitsch. anal. Chem.*, 1917, **56**, 273—298. Compare Gsell, A., 1916, ii, 584).—In certain cases, the authors have been unable to obtain results agreeing with those recorded by Gsell (*loc. cit.*), and they point out that it is necessary to have a graph of the absorption bands exhibited by the various phthaleins in order to identify the phenol from which the phthalein was prepared. The absorption spectra should also be recorded for aqueous (acid, alkaline, and neutral) and alcoholic solutions of the substances. Some phenols (naphthols, resorcinol, naphtharesorcinol, phloroglucinol, etc.) may be converted into their triphenylmethane derivatives before examination, others into their anthraquinone derivatives. The original should be consulted for the numerical results recorded. W. P. S.

A General Method for the Detection of Phenols in Essential Oils. Luis Guglialmelli (*Anal. Soc. Quim. Argentina*, 1917, **5**, 11—23).—Aldehydes, ketones, and phenols give characteristic colorations with sodium arsenotungstate or arsenotungstomolybdate, and on this is based a general method for detecting the presence of these compounds in essential oils. Hydrocarbons, alcohols, and ethers do not give colorations. A. J. W.

A New Bromine Method for the Estimation of Thymol, Salicylates, and similar Compounds. H. Elion (*J. Amer. Chem. Soc.*, 1917, **39**, 1513).—A claim that Seidell's method (A., 1912, ii, 696) is in principle the same as one described by the author in 1888. J. C. W.

Separation of Phytosterol and Cholesterol (from Fats and Oils) and the Digitonin-Precipitation Method of Marcusson and Schilling. J. Prescher (*Zeitsch. Nahr. Genussm.*, 1917, **33**, 481—485).—The author proposes to saponify the fat or oil by heating it with aqueous potassium hydroxide solution and potassium carbonate solution. The resulting soap is decomposed with hydrochloric acid, chloroform is added, and the chloroform solution of the fatty acids is separated, filtered, and treated at 50° with a 1% alcoholic digitonin solution. The mixture should be stirred during the precipitation with digitonin. W. P. S.

Modification of Fehling's Method for the Estimation of Sugar. Kuno Wolf (*Zeitsch. angew. Chem.*, 1917, **30**, i, 80).—Whilst the modification suggested by Lenk (see this vol., ii, 341) introduces certain errors in the estimation of reducing sugars, these are not of such magnitude as to interfere with the usefulness of the method for the estimation of sugar in urine.
W. P. S.

Estimation of Sugars. Eusebio López (*Anal. Fis. Quim.*, 1917, **15**, 248—251).—A modification of Fehling's method of sugar estimation, employing potassium cyanide. It is applicable to the estimation of dextrose, invert-sugar, maltose, and lactose.
A. J. W.

Estimation of Sugar. N. Schoorl and I. M. Kolthoff (*Pharm. Weekblad*, 1917, **54**, 949—953).—A review of methods of estimating sugar in which the use of potassium iodide is avoided or the amount of the salt required is small. A. J. W.

Rapid and Accurate Method of Estimating Dextrose. James Burmann (*Schweiz. Apoth. Zeit.*, 1917, **55**, 196—199; from *Chem. Zentr.*, 1917, ii, 84).—The method is intended mainly for the analysis of urine, and avoids complex apparatus by using a normal drop counter and a graduated test-tube. The Fehling's solution is of such concentration that 2 c.c. = 0·01 gram dextrose. Two c.c. of this solution are heated to boiling and the urine added drop by drop from the drop counter, with constant heating of the mixture, until the blue colour just disappears and the yellow coloration (action of alkali on sugar) is formed. Per cent. dextrose = number of drops used : 200. If the change of colour occurs before the fifth drop is added, the urine should be suitably diluted. H. W.

Estimation of Dextrose in Muscular Tissue. RALPH HOAGLAND (*J. Biol. Chem.*, 1917, **31**, 67—77).—The muscular tissue is extracted with boiling water and the extract treated with excess of phosphotungstic acid. After filtration, and removal of the excess of phosphotungstic acid by means of potassium chloride, the dextrose in the filtrate is estimated in the usual way. The author claims that this procedure removes creatinine and all reducing substances other than dextrose from the muscle extract. H. W. B.

***o*-Tolylhydrazine, a new Characteristic and Sensitive Reagent for *d*-Galactose.** A. W. VAN DER HAAR (*Rec. trav. chim.*, 1917, **37**, 108—110).—With *o*-tolylhydrazine in alcoholic solution, *d*-galactose gives an *o-tolylhydrazone*, colourless needles, m. p. 176°, after warming on a water-bath for half an hour. Neither *l*-arabinose, xylose, rhamnose, fucose, dextrose, mannose, nor lævulose gives a hydrazone with *o*-tolylhydrazine even on evaporation. With this reagent, 10 parts of *d*-galactose, with 5 parts of each of the other above-mentioned sugars, dissolved in 40 parts of water, give the characteristic, crystalline hydrazone. W. G.

Estimation of Starch in Clover. TH. VON FELLENBERG (*Mitt. Lebensmittelunters. Hyg.*, 1917, **8**, 55—56; from *Chem. Zentr.*, 1917, i, 1151—1152).—The author has recently described a direct method for the estimation of starch (this vol., ii, 342). In certain cases, particularly with ground clover, difficulties are experienced in the precipitation of the starch, due to the action of protective colloids; in such cases, the following modification of the process is advocated. The substance (1 gram) is dissolved in 20 or 25 c.c. of calcium chloride solution (1 : 1); the solution is diluted to 100 c.c. and immediately filtered, since otherwise a larger amount of the disturbing substance is dissolved. Seventy-five c.c. of the filtrate are treated with a slight excess of *N*/50-iodine solution and agitated for five minutes. The residue is extracted with dilute calcium chloride solution (1 in 10; 30—40 c.c.), *N*/50-thiosulphate solution is added until it is decolorised, and the starch is again precipitated and centrifugalised; the residue is treated with a few c.c. of dilute calcium chloride solution containing a few

drops of iodine solution, filtered through a Gooch crucible, and washed with calcium chloride solution containing iodine. The process is completed as described in the previous communication.
H. W.

[Estimation of Pectin- and Lignin-Methyl Alcohol in Roots.] TH. VON FELLENBERG (*Mitt. Lebensmittelunters. Hyg.*, 1917, **8**, 1—29; from *Chem. Zentr.*, 1917, i, 1154—1155).—See this vol., i, 616.

The Inadequacy of the Basic Ferric Acetate Test for Acetates. LOUIS J. CURTMAN and BEN R. HARRIS (*J. Amer. Chem. Soc.*, 1917, **39**, 1315—1317).—Systematic observations have been made with a view to devise a definite procedure for the detection and approximate estimation of acetates by the formation of basic ferric acetate. The results show that this is not sufficiently sensitive for general use in the detection of acetates, and that it does not afford an approximate method for estimating the quantity of acetate present in a given solution. H. M. D.

Rapid Process for the Estimation of the Higher Fatty Acids and Soaps in Fæces. JOHN SMITH SHARPE (*Biochem. J.*, 1917, **11**, 96—100).—For the estimation of the total fatty acids, including those combined as neutral fats and soaps, as well as those present in the free state, 1 gram of the thoroughly mixed material is boiled for fifteen minutes with 50 c.c. of a 2% alcoholic potassium hydroxide solution. After cooling, the solution is made up to 200 c.c. and filtered. Of the filtrate, 2 c.c. or 5 c.c., depending on the quantity of fatty acid present, are mixed with 5 c.c. of hydrochloric acid and diluted to 50 c.c. with water. A standard is prepared, as nearly as possible at the same time, by taking 2 c.c. or 4 c.c. of a standard fatty acid solution (1 c.c.$=$0·0005 gram of fatty acids), made by boiling oleic acid, 50%, palmitic acid, 25%, and stearic acid, 25%, with alcoholic potassium hydroxide, and treating with hydrochloric acid in the same way as the sample. After bringing to the same volume, both solutions are allowed to remain for five minutes, and the clouds which have then developed are compared in a nephelometer (compare Kober and Graves, A., 1915, ii, 837).

The soluble sodium and potassium soaps are first extracted with water and then estimated by the method described above. The insoluble calcium and magnesium soaps are estimated indirectly by subtraction of the amount of soluble soaps from that of the total soaps, the latter being calculated from the difference between the total fatty acids as estimated above and the free fatty acids extracted by Soxhlet's method. H. W. B.

Detection of Small Quantities of Oxalic Acid in Wine. A. A. BESSON (*Chem. Zeit.*, 1917, **41**, 642—643; *Schweiz. Apoth. Zeit.*, 1917, **55**, 81—85).—The following results have been obtained during an investigation of the method of Kreis and Baragiola (A., 1916, ii, 158). The relative concentration of the reagents has an influence, not only on the form of the oxalate crystals, but also on the sensitiveness of the reaction. The process is simple and trustworthy. A further simplification can be effected by the employment of stock solution prepared by dissolving crystalline calcium chloride (20 grams) in water (250 c.c.), adding acetic acid (250 c.c.), and cold, saturated sodium acetate solution (500 c.c.). Ten c.c. of this solution (filtered, if necessary) are added to 50 c.c. of wine, and the test is then performed according to Kreis and Baragiola's directions.

Oxalic acid, even in amounts as small as 0·01%, appears to exert a protective action against moulds. It has been further observed that wines which when first tested show a distinct reaction for oxalic acid, appear to be free from this substance after some weeks; the acid appears therefore to resemble malic acid in that it is gradually decomposed. H. W.

The Estimation of Succinic Acid. EGERTON CHARLES GREY (*Bull. Soc. chim.*, 1917, [iv], **21**, 136—141; *Biochem. J.*, 1917, **11**, 134—138).—Pasteur's method for the estimation of succinic acid is satisfactory if certain precautions are taken. The concentration of the solution of the calcium salts of the mixed acids must be effected slowly in a flask with a long neck placed in an oven at a temperature just above 100°. The presence of peptone is likely to cause a large error in the results obtained for succinic acid. Glycerol causes a much smaller error, and dextrose does not interfere with the estimation. The author finds it better to estimate the total calcium and the calcium in the filtrate after the precipitation of the calcium succinate by alcohol. The amount of succinic acid present is thus arrived at by difference. W. G.

Volumetric Estimation of Zinc Phenolsulphonate. GUIDO ADANTI (*Boll. chim. farm.*, 1917, **56**, 317—318).—In the presence of bromine and an acid, zinc phenolsulphonate reacts in accordance with the following equations: $(OH\cdot C_6H_4\cdot SO_3)_2Zn,7H_2O + H_2SO_4 = ZnSO_4,7H_2O + 2OH\cdot C_6H_4\cdot SO_3H$ and $2OH\cdot C_6H_4\cdot SO_3H + 12Br = 2C_6H_2Br_3\cdot OH + 6HBr$.

Exactly 0·5 gram of the crystallised zinc phenolsulphonate is dissolved in water and the solution made up to 500 c.c. In a flask holding about 300 c.c. and fitted with a ground stopper, 50 c.c. of this solution are mixed with 50 c.c. of 0·6% potassium bromide solution and 50 c.c. of 0·1671% potassium bromate solution, 5 c.c. of concentrated sulphuric acid being then added, and the flask again shaken and left closed in a dark place at about 25° for three hours. Ten c.c. of 10% potassium iodide solution, recently prepared, are next added, and, after the lapse of an hour, the iodine liberated is determined by titration with *N*/10-sodium thiosulphate. The number of c.c. of the thiosulphate used is subtracted from that required in a blank test with the 50 c.c. of bromide and 50 c.c. of bromate alone; the remainder, multiplied by 0·00447, gives the weight in grams of crystallised zinc phenolsulphonate in the 50 c.c. of solution taken. T. H. P.

Modifications of the Colorimetric Estimation of Uric Acid in Urine and in Blood. L. JEAN BOGERT (*J. Biol. Chem.*, 1917, **31**, 165—171. Compare Benedict and Hitchcock, A., 1915, ii, 602).—The author directs attention to the errors which arise in the application of the Benedict-Hitchcock-Folin method for the estimation of uric acid in urine, owing to variations in the rates of development and fading of colour in the standard and unknown solutions after the addition of the necessary reagents. They recommend that the standard solution should be left for fifteen minutes before being used in order to allow the point of maximum colour to be reached. Afterwards, allowance is made for a loss of colour at the rate of 5% per hour. The colour of the unknown solution should be measured at intervals of two to three minutes until the maximum colour has been developed.

The author also recommends the omission of the precipitation by colloidal iron in the method for the estimation of the uric acid in the blood. He states that the proteins of the blood can be sufficiently removed by treatment of the blood with dilute acetic acid and heat. H. W. B.

Estimation of Dicyanodiamide in Nitrolime. G. HAGER and J. KERN (*Zeitsch. angew. Chem.*, 1917, **30**, i, 53—54).—Five grams of the sample are shaken for some hours with 100 c.c. of 95% alcohol, the mixture is filtered, and two portions of 50 c.c. each are placed in separate beakers and diluted with about 150 c.c. of water. In one solution the cyanamide is precipitated by silver nitrate and ammonia. A few drops of sodium phosphate solution may be added to accelerate the precipitation; the precipitate is then collected, washed, and the nitrogen in it estimated by Kjeldahl's method. The other solution is treated with silver nitrate, and the mixture rendered distinctly alkaline by the addition, drop by drop, of 5% sodium hydroxide solution. The cyanamide and dicyanodiamide are thus precipitated together. The nitrogen is also estimated in this precipitate, and the difference between the amounts of nitrogen in the two precipitates gives that present as dicyanodiamide. W. P. S.

The Detection of Cryogenine in Urines. ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1917, [vii], **16**, 52).—Cryogenine is readily detected in urine by the following method. To 10 c.c. of the urine are added an equal volume of water and up to 1 c.c. of a 20% solution of mercuric acetate. If the urine contains cryogenine, a characteristic, salmon-pink precipitate is formed. W. G.

Microchemical Reactions of Sparteine. O. TUNMANN (*Apoth. Zeit.*, 1917, **32**, 100—103; from *Chem. Zentr.*, 1917, i, 917—918).—A 1—2% sparteine solution immediately gives with a drop of dilute chromic acid a pale yellow precipitate consisting of small droplets, which are converted after a short time into a mass of colourless needles which speedily become straw-yellow. Single, well-defined prisms are also formed. 0·1 mg. of the alkaloid yields after some time crystals united to form lattices, which slowly become transformed into prisms. The crystals polarise strongly and show extinction parallel to the long axis. The limit of sensitiveness is 50 μg. With concentrated zinc chloride solution (1 : 1), a white precipitate is formed which, under the microscope, is found to consist of aggregates of short rods. The crystals are colourless and shine feebly between crossed Nicols. In presence of a trace of hydrochloric acid, the white turbidity does not appear, but, after fifteen minutes, individual prismatic crystals are formed which show marked polarisation colours and extinction parallel to the long axis. Limit of sensitiveness, 0·4—0·3 μg. The reaction with silicotungstic acid is useless for microchemical purposes. When the alkaloid is warmed with copper chloride solution (4%) and hydrochloric acid, long, lemon-yellow prisms are gradually formed, which shine in all colours between crossed Nicols, have direct extinction and fairly strong pleochroism. The excess of copper chloride (which is usually only deposited when the solution is completely evaporated) appears as colourless or pale green needles or prisms. The reaction is not very sensitive. With mercuric chloride and hydrochloric acid, a white precipitate is formed, which is converted into rhombic prisms. With small amounts of alkaloid, the precipitate does not appear, but, after twenty to thirty minutes, individual prisms are formed. These polarise strongly and generally exhibit direct extinction; they are insoluble in alcohol and glycerol. Limit of sensitiveness, 30—40 μg. The reaction with zinc chloroiodide solution has been described previously (this vol., ii, 346). Hydriodic acid gives a dark brown to black precipitate; under the microscope, long, blackish-brown prisms or brown or red aggregates appear after some hours. The crystals shine red in polarised light, have extinction parallel to the long axis, and marked pleochroism. They are readily soluble in alcohol and attacked by glycerol. Limit of sensitiveness, 5—3 μg. Potassium iodide gives a brown precipitate, which is soon converted into brownish-black nodules, from which paler, prismatic needles are formed. Limit of sensitiveness, about 5 μg. Potassium bismuth iodide yields a yellow or yellowish-red precipitate unsuited to diagnosis. Potassium cadmium bromide [cadmium bromide (1 gram), potassium bromide (2 grams), water (7 grams)] yields colourless, flat prisms, which are converted into dendritic aggregates; they shine slightly grey between crossed Nicols. In addition, rhombic platelets and brown globules are formed. The crystal forms are very diverse. The crystals are insoluble in glycerol. Limit of sensitiveness, 8—5 μg. H. W.

Estimation of Theobromine. NORAH RADFORD (*née* ELLIOTT) and G. BREWER (*Analyst*, 1917, **42**, 274—276).—The theobromine is precipitated as its silver compound and the quantity of nitrogen in the latter is estimated. A weighed quantity of the sample (for example, crude theobromine) is dissolved in water and 5 c.c. of ammonia (D 0·880), the solution is boiled, and a hot solution containing 5 grams of silver nitrate is added. The boiling is continued until the volume of the solution is reduced to about 10 c.c. The precipitate which forms is collected, washed until free from soluble silver salts, and the nitrogen in the precipitate is then estimated by Kjeldahl's method. The number of c.c. required to neutralise the ammonia produced is calculated into terms of theobromine. The presence of large quantities of caffeine does not interfere with the estimation, since this alkaloid is not precipitated under the above conditions. W. P. S.

Replacement of Acetic Acid in Chemical Investigations. THEKLA BÄCK (*Wien. Klin. Woch.*, 1917, **30**, 465; from *Chem. Zentr.*, 1917, ii, 41—42).—In the detection of albumin in urine by the potassium ferrocyanide reaction, acetic acid may be replaced by $N/10$-hydrochloric or sulphuric acid; the volume of acid used is equal to that of the urine. More concentrated acid is to be avoided. In Weber's reaction, the fæces may be treated with 20% sulphuric acid instead of glacial acetic acid until strongly acid to Congo-red; an excess or prolonged action of acid is detrimental. It is advisable to form a lower layer of guaiacum tincture and perhydrol. With acid gastric juice, the reaction does not succeed immediately, and the juice should be exactly neutralised before acidification. This applies also to fermented fæces. Hydrochloric acid is unsuitable; the fuming acid shows the reaction, but without sufficient sensitiveness. Hydrochloric acid is also less suitable than sulphuric acid in the sodium nitroprusside test for acetone. The red coloration of creatinine is stable in the presence of acetone when 25% sulphuric acid is used (it does not become cherry-red as with acetic acid), but disappears when acetone is absent. With concentrated sulphuric acid, the red coloration becomes green in the presence of acetone. H. W.

Detection of Albumin by Bleaching Powder Solution and Hydrochloric Acid. POTJAN and STEFFENHAGEN (*Deutsch. med. Woch.*, 1917, **43**, 530; from *Chem. Zentr.*, 1917, ii, 42).—A few c.c. of urine are slowly added to a mixture of bleaching powder solution (5%; 4—6 c.c.) with two drops of pure hydrochloric acid. In the presence of albumin, an immediate, blue, opalescent turbidity is produced in which the albumin, according to the quantity, is more or less densely coagulated. Less than two drops of hydrochloric acid do not ensure the complete solution of the alkaline earths. The reaction is as sensitive as the acetic acid–potassium ferrocyanide or the sulphosalicylic acid test. It can be directly applied to cloudy urine, since the opalescence or precipitate is readily recognised even in these circumstances.

H. W.

General and Physical Chemistry.

Limiting Frequency in the Spectra of Helium, Hydrogen, and Mercury in the Extreme Ultra-violet. O. W. Richardson and C. B. Bazzoni (*Phil. Mag.*, 1917, [vi], **34**, 285—307).—The frequency of the shortest vibrations which are emitted by the molecules of helium, hydrogen, and mercury under the influence of electron impacts has been determined by a method of experiment which has enabled the authors to extend the ultra-violet region of observation considerably beyond the limits reached by Schumann and by Lyman. In the arrangement of apparatus, by which this extension is rendered possible, the thermionic radiation from a tungsten filament is allowed to fall on a metallic target under the influence of a measured difference of potential, and the velocity of the photoelectric electrons emitted is measured. This is effected by observing the strength of the magnetic field required to bend the path of the electrons into a circle of known radius, a method similar to that previously used by Ramsauer in investigating the velocity distribution of photo-electrons.

The results obtained for the three gases show that the helium spectrum extends to a limit which lies between $\lambda=470$ and $\lambda=420$ Å., and is probably near to the latter value. The hydrogen spectrum terminates at a wave-length between $\lambda=830$ and $\lambda=950$ Å., the limit being probably close to λ 900. The limit of the mercury spectrum lies between λ 1000 and λ 1200. These limits are independent of the applied potential up to 800 volts provided that this potential exceeds a certain lower limiting value.

The observed limiting frequencies of the three spectra appear to be in satisfactory agreement with the frequencies which are calculated from Bohr's theoretical values of the ionisation potentials of the respective gases, and bear no obvious relation to the ionisation potentials determined experimentally by Franck and Hertz.

H. M. D.

Origin of the Line Spectrum Emitted by Iron Vapour in the Explosion Region of the Air-Coal-gas Flame. G. A. Hemsalech (*Phil. Mag.*, 1917, [vi], **34**, 221—242).—In a previous paper (this vol., ii, 61), it was shown that there are two different types of iron cone lines, and experiments are now described in which the conditions governing the emission of these lines have been more fully investigated.

The changes produced in the spectrum by varying the composition of the gas mixture, by changing the atmosphere in which combustion takes place and by reversal, lead to the conclusion that nitrogen is essential for the emission of the characteristic cone spectrum of iron. It is suggested that the nitrogen combines with the iron to form a nitride, this reaction being directly responsible for the cone lines. The formation of this nitride appears, however, to depend on the presence of oxygen in the medium surrounding the air–coal-gas flame. If ammonia is present in the air–coal-gas and oxy-coal-gas flames, the nitride is formed less readily.

When an air–coal-gas flame is heated electrically by means of a graphite rod, the intensities of the iron lines are only slightly increased. The cooling of the flame brings about a diminution in the intensities.

The behaviour of the iron lines emitted by the mantles of various flames is such as to suggest that they are largely influenced by the temperature. The absence of the supplementary iron spectrum from the cone emission of the oxy-hydrogen and oxy-acetylene flames cannot be accounted for by the higher velocity of these flames. H. M. D.

Absorption Bands of Atmospheric Ozone in the Spectra of Sun and Stars. A. Fowler and (Hon.) R. J. Strutt (*Proc. Roy. Soc.*, 1917, *A*, **93**, 577—586).—The spectrum of Sirius exhibits a group of lines near the limit of atmospheric transmission which were first described by Huggins (*ibid.*, 1890, **48**, 216). The examination of a more recent photograph of the spectrum has shown that the lines really represent a system of bands. The supposition that these bands are due to atmospheric absorption is supported by the fact that the same bands are found in the spectra of a number of stars and also in the spectrum of the low sun.

A comparison of the bands with those found in the spectrum of ozone, which has been re-examined in this connexion, shows that the atmospheric constituent responsible for the production of these bands in the solar and stellar spectra is undoubtedly ozone.

H. M. D.

Absorption Spectra of Substances containing Conjugated and Unconjugated Systems of Triple Bonds. Alexander Killen Macbeth and Alfred Walter Stewart (T., 1917, **111**, 829—841).—The fact that the absorptive power of saturated substances is less than that of the corresponding ethylenic derivatives, and that conjugation of double bonds in diethylene derivatives is accompanied by an increase in the absorptive power, has led the authors to inquire whether a similar relation obtains in the case of acetylenic derivatives.

Acetylenic compounds belonging to both aliphatic and aromatic series were examined, but the absorption spectra show that there is no close parallelism between the light-absorbing capacities of acetylenic and analogous ethylenic derivatives, and that the above generalisation is not applicable to substances containing conjugated and unconjugated systems of triple bonds.

The observations afford further evidence, however, with regard to the influence which is exerted by residual affinity on the absorptive power, and an attempt is made to formulate this in general terms. H. M. D.

Effect of Additional Auxochromes on the Colour of Dyes. II. Triphenylmethane- and Azo-dyes. PRAPHULLA CHANDRA GHOSH and EDWIN ROY WATSON (T., 1917, **111**, 815—829).—The absorption bands in solutions of different concentrations were determined by observing the positions of the edges of the bands with an ordinary spectroscope, as in the previous investigation of the xanthene and anthraquinone groups of dyes (T., 1915, **107**, 1581; 1916, **109**, 544).

In some cases, the multiplication of auxochromes has but little influence on the position of the bands, the only effect observed being a strengthening and broadening of the bands. In other cases, the bands are shifted to a considerable extent, but remain of about the same breadth, whilst in yet other cases additional bands make their appearance. Even in the same series, very diverse effects have been observed, and the authors conclude that more material is required before any explanation of the effects produced by multiplication of auxochromes can be attempted.

H. M. D.

Production of Coloured Flames of High Luminosity for Demonstration and Experimental Purposes. G. A. HEMSALECH (*Phil. Mag.*, 1917, [vi], **34**, 243—245).—The apparatus described affords a ready means of obtaining highly luminous, coloured flames with either the electric or Gouy sprayer, and makes use of the fact that the admixture of oxygen to the gases feeding an air–coal-gas flame greatly intensifies the flame lines. The arrangement is such that the flame can be fed in succession with the sprays from a number of different solutions without any re-adjustment of the gas mixture. H. M. D.

The Nomenclature of Radio-elements. K. FAJANS (*Zeitsch. Elektrochem.*, 1917, **23**, 250—257).—The chaotic state of radioactive nomenclature is discussed, and all the various names used for the same members of the disintegration series by different writers set forth. This is particularly confusing in the case of the branch series starting from the three C-members. It is suggested that, pending an international revision of the nomenclature, the names first used should be employed. The difference in the names in use is often slight, as, for example, in the suffixes I and II, or 1 and 2, applied to mesothorium. The following is the nomenclature, according to the principle recommended, in the cases where more than one name is in vogue: uranium I and II, uranium X_1 and X_2, mesothorium 1 and 2. For the C-members and their branch products, the parent C-member is designated C_1 in each case, whilst RaC' and RaC_2, AcC_2 and AcD, ThC_2 and ThD, are respectively the α- and the β-ray-giving products in the two branches. In symbols, the prefix "radio" is to be designated by Rd, not Ra; thus RdTh for radiothorium.

For future readjustment of the nomenclature, the suggestion is made to designate by the index l, meaning lateral, the first branch product, and by m, n, etc., later products of the branch. Thus RaC_1^l would stand for what above has been termed RaC_2 (and RaC_2 for what has above been termed RaC'), and RaC_1^m for the still unknown product of RaC_1^l. This is to apply to all three series, although in the actinium series AcC_1^l would denote the main product rather than the branch product. The almost insuperable difficulties in the way of a consistent and at the same time convenient and suggestive nomenclature are considered with great thoroughness. F. S.

The X-ray Spectra of Isotopic Elements. MANNE SIEGBAHN and W. STENSTRÖM (*Compt. rend.*, 1917, **165**, 428—429).—A comparison of the X-ray spectra of the isotopes, lead and radium-G, shows that the wave-lengths of the lines in the series L, and α and β in series M, agree to within about 0.0001×10^{-8} cm. for the two isotopes. W. G.

Potential of the Lead Electrode. GILBERT N. LEWIS and THOMAS B. BRIGHTON (*J. Amer. Chem. Soc.*, 1917, **39**, 1906—1912).—The electrode potential of lead has been measured in saturated solutions of lead chloride, bromide, and iodide. From the results obtained with the iodide solution, the normal potential is found to be 0·4125 against the normal calomel electrode and 0·1295 against the normal hydrogen electrode.

The saturated solution of lead iodide at 25° is 0·00165 mol. per litre, which gives $11 \cdot 9 \times 10^{-9}$ for the ionic solubility product. The ionic solubility products of lead bromide and lead chloride, which are calculated from the electrode potentials in the saturated solutions of the two haloids, differ considerably from those which are given by the usual method of deriving this quantity. H. M. D.

Dilatometer for Measuring the Absolute Dilatation of Liquids. JEAN ESCARD (*Ann. Chim. anal.*, 1917, **22**, 169).—The apparatus consists of a 1-litre copper flask enclosed in a 2-litre glass flask; the space between the walls of the two flasks holds 1 litre. The necks of the flasks are elongated, and the outer one is graduated. The liquid under examination is filled into the space between the two flasks, and the dilatation with rise of temperature is observed by the rise in the level of the liquid in the graduated neck. The cubical dilatation of the two vessels is determined before the instrument is used. W. P. S.

Fenchone in Cryoscopy. TEMISTOCLE JONA (*Gazzetta*, 1917, **47**, ii, 87—98).—The paper records the results obtained in cryoscopic investigations of thirty-two organic substances, using fenchone as the solvent. The mean value of K for fenchone, calculated from the results obtained with twenty-one of these substances, is 68·10. R. V. S.

The Viscosity of Liquids. II. The Viscosity-Composition Curve for Ideal Liquid Mixtures. JAMES KENDALL and KENNETH POTTER MONROE (*J. Amer. Chem. Soc.*, 1917, **39**, 1787—1802. Compare A., 1914, ii, 109).—The question of the connexion between the viscosity and the composition of ideal binary mixtures has been examined by experiments with mixtures of benzene and benzyl benzoate, benzene and ethyl benzoate, toluene and ethyl benzoate, and of toluene and benzyl benzoate. The components of each of these pairs of liquids differ widely both with respect to viscosity and molecular weight, and the observations afford in consequence a stringent test of the various formulæ which have been put forward to express the relation between the viscosity and the composition of ideal mixtures. The data are considered more particularly with reference to the nine formulæ which result when the simple mixture rule is applied to the viscosity, fluidity, or logarithmic viscosity, and the composition expressed in terms of weight, volume, or molecules, and it is found that none of these equations is in approximate agreement with the facts. On the other hand, the results obtained for the first three pairs of liquids agree closely with those calculated from the formula $\eta^{\frac{1}{3}} = x\eta_1^{\frac{1}{3}} + (1-x)\eta_2^{\frac{1}{3}}$, in which x and $1-x$ are the molar fractions of the two components, the viscosities of which are η_1 and η_2 respectively. For mixtures of toluene and benzyl benzoate, on the other hand, the observed viscosities diverge considerably from those given by the cube root formula. H. M. D.

The Viscosity of Liquids. III. Ideal Solutions of Solids in Liquids. JAMES KENDALL and KENNETH POTTER MONROE (*J. Amer. Chem. Soc.*, 1917, **39**, 1802—1806. Compare preceding abstract).—The viscosities of mixtures of benzene and naphthalene, of benzene and diphenyl, of toluene and naphthalene, and of toluene and diphenyl have been measured at 25°, and the applicability of the cube root formula $\eta^{\frac{1}{3}} = x\eta_1^{\frac{1}{3}} + (1-x)\eta_2^{\frac{1}{3}}$ tested by calculating therefrom the viscosity η_2 of the naphthalene or diphenyl. Although the several values of η_2 for each series of mixtures are in close agreement, there is a very considerable difference between the values obtained from the benzene series of mixtures on the one hand and the toluene series on the other. Thus the mean value of η_2 for naphthalene in admixture with benzene is 0·225, whilst the toluene series of mixtures gives 0·0183 as the mean value of η_2. It may be noted, however, that the ratio of these numbers is the same for diphenyl as for naphthalene. H. M. D.

Constitution and Fundamental Properties of Solids and Liquids. II. Liquids. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1917, **39**, 1848—1906).—In a previous paper (this vol., ii, 19) the author has put forward the view that the forces acting between atoms and molecules are chemical, as distinguished from physical, in character. The forces are specific in their action, have a range which is limited to atomic distances, and act only in more or less definite directions determined by the degree of saturation of the neighbouring atoms. A distinction is made between forces which correspond with primary and secondary valence, but it is claimed that these types, both of which are strictly chemical, suffice for the explanation of cohesion, evaporation, crystallisation, adsorption, surface tension, viscosity, and other properties of liquids.

This theory of chemical forces is further developed in the present paper and applied to a series of observations which have been made on the properties of liquid surfaces.

The experiments made by Rayleigh, Marcelin, and Devaux on the spreading of oils on the surface of water have been extended. The spreading is attributed to the presence of an active group in the molecule of the oily substance, this active group having a marked affinity for water. The chemical forces which thus come into play, lead to the orientation of the oil molecules in such a way that the carboxyl groups of the molecules are all in contact or combined with water molecules, whilst the hydrocarbon chains are situated vertically above the carboxyl layer. The tendency of the oil to spread is thus attributed to the chemical forces acting between the carboxyl groups and the water molecules. It is possible to determine the cross-sections and lengths of the oriented molecules by observations of the extent to which a given weight of the oil spreads on the surface of water. Such measurements have been made for a number of substances, and it has also been found possible, by means of a special type of balance, to measure the forces which are required to compress oil films of different thicknesses. The curves obtained by plotting this force against the thickness of the film show characteristic breaks which are considered to afford confirmation of the view that the spreading of films on surfaces is determined by the configuration of the molecules and the relative activities of the different portions of the molecule.

Since adsorption is presumably a surface effect, the theory should be applicable to the explanation of phenomena which are grouped under this head. In a recent paper, Gurvich (compare A., 1914, ii, 435; 1915, ii, 744) has expressed the view that adsorption phenomena are due to physical as distinguished from chemical forces, but the author, as the result of a critical examination of the arguments put forward, arrives at the conclusion that these forces are also chemical and do not differ in any essential feature from those which give rise to the formation of typical chemical compounds. H. M. D.

The Adsorption of Carbon Dioxide and Ammonia by Charcoal. LEON B. RICHARDSON (*J. Amer. Chem. Soc.*, 1917, **39**, 1828—1848).—The equilibrium pressures (up to 300 cm. of mercury) have been measured at temperatures between −64° and 200° for the system charcoal–carbon dioxide, and between −20° and 200° for the system charcoal–ammonia. At a given temperature, the adsorption is in fair agreement, over a limited range of pressures, with the equation $a = \alpha \cdot p^{1/n}$, in which a is the volume of gas adsorbed by 1 gram of charcoal under a pressure p, α and n being constants. At higher pressures (above 60 cm.), the adsorption is less than that required by this formula, and appears to reach a maximum which at a given temperature is unchanged by further increase in the pressure. There is no evidence of a chemical action

between carbon and carbon dioxide, but at low temperatures effects are observed which suggest that part of the gas dissolves to form a solid solution.
H. M. D.

The Solvent Properties of Emulsions. Theory of Dyeing in a "Boiled off Liquor" Bath. P. Sisley (*Bull. Soc. chim.*, 1917, [iv], **21**, 155—157).—If a dilute aqueous solution of phenosafranineazonaphthol, slightly acidified with acetic acid, is gently shaken with chloroform, no emulsion being formed, the colouring matter is divided between the water and chloroform according to a definite partition-coefficient. If, however, the chloroform is emulsified, the colouring matter accumulates in the emulsified portion and the water is almost decolorised. If the tube is left, the unstable emulsion gradually breaks down and the colouring matter returns to the water. This phenomenon can be repeated indefinitely. On the basis of this, the author explains the dyeing of silk with almost insoluble dyestuffs in a "boiled off liquor" bath. A similar explanation may be given for the dyeing of cotton, using an oil emulsion as mordant, and the dyeing of leather in a fatty bath.
W. G.

A Complete Review of Solutions of Oceanic Salts. I and II. Ernst Jänecke (*Zeitsch. anorg. Chem.*, 1917, **100**, 161—175, 176—236. Compare A., 1906, ii, 833; 1907, ii, 278, 480, 702).—I. The author discusses the different methods of representing graphically the solubility relations of reciprocal salt pairs, with special reference to the system $2KCl + MgSO_4 \rightleftharpoons MgCl_2 + K_2SO_4$.

II. The author's graphic method of representation is applied to "doubled-ternary" systems, that is, systems comprising six different salts, as, for example, $(Na_2,K_2,Mg)(Cl_2,SO_4)$. A quantitative graphic representation has been devised for this system, in the special case of complete saturation with sodium chloride, for the range of temperature between 0° and 120°. Numerous diagrams are given, for the interpretation of which the original must be consulted.
E. H. R.

The Uniform Movement of Flame in Mixtures of Acetylene and Air. William Arthur Haward and Sosale Garalapury Sastry (T., 1917, **111**, 841—843).—Observations made in a glass tube 12 mm. in diameter show that the maximum speed is obtained with mixtures containing 8—10% of acetylene. In the curve showing the relation between the speed and the percentage of acetylene in the mixture there is a gradual flattening towards the upper and lower limits, and the crest of the curve is also flattened. Mixtures containing more than about 20% of acetylene deposit soot, and the speed of propagation of flame in such mixtures is slow. The fact that the maximum speed is found in mixtures which contain rather more than the mixture (7·75% of acetylene) which corresponds with complete combustion, is probably due to the greater thermal conductivity of acetylene as compared with air.
H. M. D.

The Saponification of Fats. J. P. TREUB (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 35—63).—A mathematical discussion of the subject, in which it is shown that in the saponification of an emulsion, the reaction takes place chiefly at the boundary of the two phases, the process of saponification being governed by the value of the surface tensions between the glycerides and the saponifying medium. Equations were derived giving the relation between separated fatty acid and separated glycerol, and it was found that those equations in which the increase of concentration of the lower glycerides at the surface of contact between fat and water phase was taken into account appeared to explain the different course of the saponification in different surroundings.
W. G.

Sulphonation of Quinol. II. JOH. PINNOW (*Zeitsch. Elektrochem.*, 1917, **23**, 243—249. Compare A., 1915, i, 883).—A continuation of the previous work; the kinetics of the sulphonation of quinol have been studied at 100°, 80°, 60°, and 50° by a slightly modified method, using sulphuric acid from $7\cdot82M$ to $13\cdot39M$. It is shown that if quinol is added to sulphuric acid in such quantities (1—2%) that the total volume is practically unchanged, the logarithm of the velocity of sulphonation increases proportionally to the concentration of the acid. For unit increase in the molarity of the acid, the increase in the logarithm is 0·643 at 60°, 0·612 at 80°, and 0·606 at 100°. The logarithm of the velocity for $7MH_2SO_4$ is $\bar{4}\cdot500$ at 60°, $\bar{5}\cdot655$ at 80°, and $\bar{6}\cdot637$ at 100°. The equilibrium between quinol, quinolmonosulphonic acid, and aqueous sulphuric acid moves toward the sulphonic acid with decreasing temperature. The temperature-coefficient of the formation and hydrolysis of quinolmonosulphonic acid increases with decreasing concentration of sulphuric acid. The hydrolysis depends chiefly on the monohydrate of sulphuric acid, as was previously shown to be the case in the formation of the monosulphonic acid.
J. F. S.

The Positive Nucleus of the Atom. A. HAAS (*Physikal. Zeitsch.*, 1917, **18**, 400—402).—A theoretical paper in which the author discusses the structure of the positive nucleus with special reference to the Rutherford theory and the difficulties which are involved in the assumption that the entire mass is electromagnetic in origin. An attempt is made to meet these difficulties by a theory of atomic structure which is shown to lead directly to Moseley's formula for the connexion between the *X*-ray frequencies and the atomic numbers of the elements. H. M. D.

Problems Bearing on Residual Affinity. SPENCER UMFREVILLE PICKERING (*Proc. Roy. Soc.*, 1917, *A*, **93**, 533—549).—A theoretical paper in which the subject of residual affinity is discussed in its relation to phenomena of double decomposition and thermal data. H. M. D.

An Air-tight Gas Collecting Tube without Stopcock. Georg Wempe (*Zeitsch. angew. Chem.*, 1917, **30**, i, 208. Compare *ibid.*, 1914, **27**, i, 216).—The apparatus consists of a cylindrical vessel of 100—200 c.c. capacity, into which two glass tubes are fused which pass to the bottom of the vessel. The latter is completely filled with water; the gas is then admitted through one tube, the displaced water passing away through the other tube, the process being stopped while the ends of the tube still dip beneath the water. To discharge the gas, the vessel is placed in a horizontal or inclined position; water is admitted through one tube, the gas passing out through the other. H. W.

When Did the Alchemists Jan Isaac of Holland and Isaac of Holland Live? Hermann Schelenz (*Zeitsch. angew. Chem.*, 1917, **30**, i, [65], 195—196).—Lippmann (A., 1916, ii, 525), in a passage from Ben Jonson's "The Alchemist," finds support for the suggestion that at the time of publication of the play, which he sets at 1610, Jan Isaac, the father, was but recently dead, whilst Isaac, the son, was still alive, and, further, that the writings of the two only appeared in print subsequently to 1600. The author objects that these conclusions are based on an imperfect translation, and that Ben Jonson's works were not printed until 1616. To judge from the authorities cited by him, Jan Isaac probably belonged to the fifteenth century—anterior to Hohenheim-Paracelsus, whom he does not mention. Jorissen (*Chem. Weekblad*, 1917, **14**, 304) states that Hugo de Groot, "Parallelon Rerum, etc.," 1602, says Jan Isaac lived 160 years before that date. Jorissen, amongst other references, also cites Lenglet du Fresnoy (1742) in favour of the view that, contrary to the usual opinion, Jan Isaac was the son of Isaac (compare also Holgen, this vol., ii, 461). T. S. Pa.

Isaac of Holland and Jan Isaac of Holland. W. P. Jorissen (*Chem. Weekblad*, 1917, **14**, 897—903).—A further contribution to the discussion as to the period of these alchemists (compare preceding abstract). A. J. W.

Inorganic Chemistry.

Hydrogen Peroxide. V. Macri (*Boll. chim. farm.*, 1917, **56**, 417—418).—Hydrogen peroxide prevents the precipitation of phosphomolybdate when solutions of ammonium molybdate and phosphoric acid are mixed. Hydrogen sulphide does not affect the reaction between hydrogen peroxide and chromic acid if the chromic acid is added to the solution of hydrogen peroxide and hydrogen sulphide. When hydrogen peroxide is treated with ammonia in presence of calcium chloride, a precipitate, CaO_2, is formed. When hydrogen peroxide is evaporated in a platinum dish in the presence of hydrogen chloride, a certain amount of chloroplatinic acid is formed.

The estimation of free acid in hydrogen peroxide may be effected by titration with permanganate, the end-point being shown by the appearance of a brownish-yellow coloration. R. V. S.

Preparation of Chlorine Gas. THE SOLVAY PROCESS Co. (U.S. Pat., 1236570, 1917; from *J. Soc. Chem. Ind.*, 1917, **36**, 1048).—An alkali chloride is heated with ferric sulphate in the presence of oxygen. The ferric sulphate is formed by treating ferric oxide mixed with sodium chloride with sulphur trioxide at a temperature below that at which chlorine compounds are evolved. H. W.

Liberation of Hydrogen Sulphide from Gob Fires in Coal Mines. THOMAS JAMES DRAKELEY (T., 1917, **111**, 853—863).—According to Lewes, sulphur would be liberated in the form of sulphur dioxide if the spontaneous heating of coal was in any way connected with the presence of iron pyrites. Experiments are described which show that hydrogen sulphide is formed by passing sulphur dioxide over heated coal, by heating mixtures of coal and sulphur or mixtures of coal and iron pyrites, and by passing dry or moist hydrogen or moist carbon dioxide over heated iron pyrites. Comparison of the figures obtained in the action of dry and moist hydrogen on iron pyrites shows that the presence of water vapour favours the production of hydrogen sulphide.

In view of these observations it is improbable that the sulphur dioxide formed at the seat of a gob fire would find its way into the mine atmosphere. If not completely reduced to hydrogen sulphide by contact with heated coal in the vicinity of the fire, it would encounter hydrogen sulphide evolved by the heated material in the locality, and would thereby be reduced with the production of sulphur. H. M. D.

Action of Hydrogen on Sulphuric Acid. FRANCIS JONES (*Mem. Manchester Phil. Soc.*, 1917, **61**, No. 3, 1—3).—In the bulb of a non-tubulated retort, the open end of the neck of which dips under water, is placed some strong sulphuric acid, the remainder of the retort being filled with pure hydrogen. When the whole is left at the ordinary temperature for a few days the water gradually rises in the neck of the retort, owing to reduction of the sulphuric acid by the hydrogen with formation of sulphur dioxide (compare Milbauer, A., 1907, ii, 252). T. S. P.

Removal of Nitric Acid from Solutions of Organic Compounds. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1917, **31**, 599—604).—To remove nitric acid from organic mixtures the acidity of the solution is first estimated by titration of a small sample and the solution is then neutralised by means of barium hydroxide. About 2 grams of freshly prepared aluminium amalgam are added for each gram of nitric acid and reduction of the acid allowed to proceed at the ordinary temperature for eight hours (or overnight), the solution being aerated during the entire time of reduction. The nitric acid is completely transformed into ammonia and oxides of nitrogen.

To remove the added reagents and the products of reduction, the mixture is filtered from the aluminium and mercury, and the filtrate treated with slight excess of barium hydroxide. By concentration under diminished pressure, the ammonia is removed, and the barium is then quantitatively precipitated with sulphuric acid.

The aluminium amalgam is prepared by immersing sheets of aluminium foil in a 3% solution of mercuric chloride. In a few minutes the surface of the foil is covered with mercury. The foil is immediately washed in running water and transferred at once to the nitrate solution. H. W. B.

The Melting Points of the Chlorides of Lithium, Rubidium, and Cæsium, and the Freezing Points of Binary and Ternary Mixtures of these Salts, including also Potassium and Sodium Chloride. THEODORE W. RICHARDS and W. BUELL MELDRUM (*J. Amer. Chem. Soc.*, 1917, **39**, 1816—1828).—From cooling curves the melting points obtained are lithium chloride, 613°, rubidium chloride, 714°, cæsium chloride, 645°. The lithium and cæsium chlorides were unusually pure, but the rubidium salt probably contained small quantities of impurities.

The freezing-point diagram for mixtures of potassium and lithium chloride is of the simplest type, the curves meeting at 358°. Eutectic temperatures were found for rubidium and lithium chlorides at 318° and for cæsium and lithium chlorides at 323°, but in both cases the diagram affords evidence of the existence of a 1:1 compound.

The freezing points of ternary mixtures of lithium and sodium chlorides with each of the three other alkali chlorides were also determined. H. M. D.

The Nature of Subsidiary Valencies. XV. Polyhaloids. FRITZ EPHRAIM (*Ber.*, 1917, **50**, 1069—1088. Compare this vol., ii, 319).—The thermal dissociation of the various alkali polyhaloids has been studied, and the temperatures determined at which the vapour pressures of the liberated halogens are equivalent to 760 mm. of mercury. The special apparatus employed is fully described, the novel feature being the device for keeping the halogen away from the mercury in the manometer.

Comparing pairs of cæsium and rubidium compounds, it is found that the ratio of the absolute temperatures of dissociation, $T_{Cs}:T_{Rb}$, is approximately constant, being about 1·12:1 for the whole group, and that the ratio $T:\sqrt{\text{atomic volume}}$ is the same for the two members of each series. Knowing the dissociation temperature for a given cæsium compound, it is therefore possible to

ability of the analogous rubidium compound. The
he most stable, and as long as one iodine atom is
er tri-haloids are not much less stable.
om would thus appear to be the central atom, and
pected, therefore, that the compound $CsICl_2$, for
decompose into cæsium iodide and chlorine. As a
it gives cæsium chloride and iodine chloride. This
be due to any secondary effect of moisture, for the
s of chloride are obtained when the substance is
horic oxide.
om the formula $T:\sqrt{v}=k$, on the basis of the
esium compounds, the following values for potass-
obtained :

KI_3.	KBr_3.	KI_2Br.	$KIBr_2$.	$KICl_2$.	$KClBr_2$.	$KClI_2$.
46·5°	66°	108·5°	142°	109°	47°	57°

therefore, the dissociation temperature is below
t of the ejected halogen. These compounds are
is obvious that they are not likely to be obtained
nperatures.
the curves connecting absolute temperature and
ure for any two compounds of substances with
run parallel. For example, the ratio,

$$T_{CsBr_3} : T_{ZnCl_2,6NH_3},$$

. . . 700 mm. is almost constantly 1 : 1·265. The
ule may therefore be employed to calculate pres-
of this kind when only one tension point has been

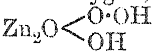
oyed in this study were prepared by Wells and
l, with modifications in some cases. The data
vapour pressures at different temperatures of the
CsI_3, $CsBrI_2$, $CsBr_2I$, $CsCl_2I$, $CsBr_3$, $CsClBr_2$,
bBr_2I, $RbBr_3$, $RbClBr_2$, $RbCl_2Br$, $RbCl_2I$, KI_3,
NH_4Br_3, NH_4Cl_2Br, and in addition cupric and
J. C. W.

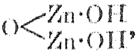
ible Error regarding the Solubility of
nate in Boiling Water. ALFREDO CAVAZZI
7, ii, 49—63).—When boiled with water, calcium
dissociates with evolution of carbon dioxide. This
at a certain point, and is prevented if a solution
xide (saturated at the ordinary temperature) is
ling suspension of carbonate in the proportion of
er litre. After prolonged boiling of calcium
er, the substance which passes into solution is
e, and the amount of it depends chiefly on the
uid, the duration of the boiling, and the concen-
olution. Small quantities of sodium carbonate
litre) prevent dissociation. When calcium
uced by chemical action in aqueous solution at a
it forms supersaturated solutions even in the

presence of calcium hydroxide; the stability of these solutions depends chiefly on the concentration and the temperature

R. V. S.

Zinc Perhydrates. [**Hydroperoxides.**] F. W. Sjöström (*Zeitsch. anorg. Chem.*, 1917, **100**, 237—248. Compare de Forcrand, A., 1902, ii, 322, 606; 1904, ii, 172; Kurilov, A., 1904, ii, 36; Ebler and Krause, 1911, ii, 801; Riesenfeld and Nottebohm, A., 1915, ii, 454).—When a solution of zinc sulphate is added to excess of a solution of sodium hydroxide containing hydrogen peroxide, the zinc is totally precipitated as hydroperoxide. The amount of hydrogen peroxide used cannot, however, be estimated volumetrically on account of its rapid decomposition in alkaline solution. For a more thorough examination of zinc hydroperoxide the following method of preparation was used.

Freshly ignited pure zinc oxide was left for several hours with the calculated quantity of 30% hydrogen peroxide solution at −10°. A product was obtained which above 2° formed a pasty mass, and when dried on a porous plate at 35—40° over soda-lime was obtained as a white powder. This was analysed by estimating active oxygen, zinc oxide, and water. It contained 8·04% active oxygen, and corresponded almost exactly with the composition  $Zn_2O{<}\begin{matrix}O\cdot OH\\ OH\end{matrix}$ Towards water, alcohol, or ether at the ordinary temperature it is quite stable, and is only slowly decomposed by 2*N*-sodium hydroxide. It does not appear, however, to be a simple chemical individual, since by trituration with water it can be separated into fractions containing varying quantities of active oxygen. Another preparation, fractionated in this manner before drying, gave three similar fractions, each containing about 12% of active oxygen and corresponding with no particular formula. Similar products were obtained by boiling zinc carbonate with excess of 30% hydrogen peroxide solution.

It is concluded that zinc perhydrate generally consists of a mixture of substances, derived from the two compounds $Zn(OH)_2$ and  $O{<}\begin{matrix}Zn\cdot OH\\ Zn\cdot OH\end{matrix}$, the hydroperoxides being of the types $OH\cdot Zn\cdot O\cdot OH$ and $Zn(OH)\cdot O\cdot Zn\cdot O\cdot OH$. Hydrogen peroxide, since it decomposes zinc carbonate, acts as a monobasic acid.

E. H. R.

Allotropy of Cadmium. Fredrick H. Getman (*J. Amer. Chem. Soc.*, 1917, **39**, 1806—1816).—The results of measurements of the *E.M.F.* of cells arranged according to the scheme $Cd\,|\,CdSO_4$ solution | 8% Cd amalgam would seem to indicate that there are two, and only two, allotropic modifications of cadmium between 0° and 100°. The initial value of the *E.M.F.* of such cells at 20° diminishes with time, but finally attains a constant value. When this condition has been attained, the *E.M.F.* decreases linearly with rise of temperature up to 40°.

When cells of the above type are maintained at 90°, the *E.M.F.* also becomes constant, but in this case the *E.M.F.* decreases linearly with fall of temperature down to 40°.

By means of formulæ which express the experimental observations, the temperature at which the *E.M.F.* reaches its minimum value is found to be 37·5°, which may be regarded as a close approximation to the transition temperature $Cd_{\alpha} \rightleftharpoons Cd_{\beta}$. H. M. D.

Decomposition of Lead Hydrogen Arsenate by Water. C. C. McDonnell and J. J. T. Graham (*J. Amer. Chem. Soc.*, 1917, **39**, 1912—1918).—Experiments are described which show that lead hydrogen arsenate is decomposed by water with the formation of a basic salt, the reaction, which is reversible, being represented by the equation $5PbHAsO_4 + H_2O \rightleftharpoons Pb_4(PbOH)(AsO_4)_3 + 2H_3AsO_4$. The concentration of arsenic acid in the equilibrium condition is very low, but if the water is continuously renewed, the lead hydrogen arsenate is completely decomposed and the residue consists of the basic lead arsenate, $Pb_4(PbOH)(AsO_4)_3,H_2O$ (hydroxy-mimetite). H. M. D.

The Nature of Subsidiary Valencies. XVI. The Intensity of the Attachment of Water in Compounds with Water of Crystallisation. Fritz Ephraim and Paul Wagner (*Ber.*, 1917, **50**, 1088—1110).—The vapour pressures of a large number of alums and sulphates of the type

$$M_2'SO_4,M''SO_4,6H_2O,$$

have been determined at different temperatures, these salts being chosen for comparative purposes because so many of them are known, the members of one class have the same constitution, and their melting points are high. The apparatus is described.

In the case of the second class of salts, the pressures rise very slowly up to a certain point, when they increase suddenly and afterwards grow normally. This lagging effect, or "period of induction" according to Rae (T., 1916, **109**, 1229), has been reported before by Ephraim, in the case of ammines (this vol., ii, 319), and is now discussed in the light of two or three theories.

The stability of the alums is greater as the volume of the anionic metal is greater, and the same holds good for the other class (schönites), except that magnesium seems to be out of place. This is due, however, to the fact that the atom of this metal occupies less space in the double sulphate molecule than the volume as calculated from its density. The influence of the cationic metal in both series is practically nothing, but the stability of the hydrates is normally greater as the atomic volume is greater, and similarly, the change from sulphates to selenates is of very little influence on the vapour pressures. In a molecule of 48 atoms it is, of course, scarcely likely that the exchange of a single atom for a similar one will have much effect on the general stability.

The molecular volume of a stable compound is always smaller than the sum of the volumes of its decomposition products, but some elements may be relatively more compressed than others. This is seen in the case of the schönites, the necessary density data having been determined by one worker, Tutton. The double magnesium sulphates have smaller molecular volumes than the copper or manganese salts, although the atomic volume of the metal is much greater than those of the other two. The stability of the salts is therefore more strictly parallel to their molecular volumes than to the atomic volumes of the free metals. What really matters in connexion with the stability of a compound is, therefore, not the actual contraction suffered by any particular atom during the formation of the compound, but the percentage contraction on the atomic volume, a method of calculation which has apparently only been introduced by Stephenson (*Chem. News*, 1911, **102**, 178, 187).

The data recorded refer to the following compounds: *aluminium* and *chromium* alums of K, NH_4, Rb, Cs, Na, Tl; *vanadium* alums of NH_4, Rb, Cs; *ferric* alums of NH_4, Rb, Cs; *titanium* alums of Rb, Cs; cæsium *manganic* and *cobaltic* alums; *selenate* alums of K–Al, Cs–Al, and Cs–Cr; double sulphates of K, NH_4, Rb, and Cs with Cu″, Ni″, Mg, and Mn″. J. C. W.

Martensite, Troostite, Sorbite. P. DEJEAN (*Compt. rend.*, 1917, **165**, 429—431. Compare this vol., ii, 477).—The author defines these three constituents of steel. For martensite he accepts Le Chatelier's definition (this vol., ii, 477). Troostite is the constituent, easily attacked by micrographic reagents, and obtained when a steel, previously heated to a temperature at least equal to that of the critical point Ac_1, is tempered with an energy insufficient to produce pure martensite. Sorbite is chemically and physically almost identical with troostite, and is obtained by thermal treatment, below the critical point Ac_1, of a steel previously tempered. It differs from troostite in its micrographic appearance.

W. G.

The Heterogeneity of Steels. H. LE CHATELIER and E. L. DUPUY (*Compt. rend.*, 1917, **165**, 349—352. Compare A., 1915, ii, 779).—The authors have modified the composition of Stead's reagent for characterising the heterogeneity of phosphorus steels, and have thus increased its sensitiveness and made it applicable to non-phosphorus steels. The reagent, as now prepared, contains alcohol (95%), 100 c.c.; water, 10 c.c.; crystalline copper chloride, 1 gram; picric acid, 0·5 gram; hydrochloric acid, 1·5—2·5 c.c. The proportions of copper chloride and picric acid may be varied from one-half to double the amounts given without modifying the results, but the proportions of alcohol and water must be rigorously adhered to. The exact acid content, which must be adjusted by trial, controls the success of the reagent. W. G.

Structure of Magnet Steel and its Change with Heat Treatment. KÔTARÔ HONDA and TAHEJIRÔ MURAKAMI (*Sci. Reports, Tôhoku Imp. Univ.*, 1917, [i], **6**, 53—70).—Four specimens of magnet steel have been investigated by thermal, magnetic, and microscopic methods. It has been found that thermal analysis is not so convenient a method for detecting minute changes in structure as is magnetic analysis. A change which is recorded by the thermal method is also easily detected by the magnetic method, and it is possible exactly to locate the transformation, but there are changes associated with the development or absorption of only very small amounts of heat which cannot be detected by thermal methods, whilst magnetic methods give good results.

The specimens of magnet steel gave the following analyses:

Specimen.	C.	P.	S.	Mn.	Si.	W.
Böhler	0·47	0·016	0·016	0·20	0·24	5·38
Swedish	0·59	0·015	trace	0·20	0·23	4·82
Yonago	0·61	—	—	—	0·27	4·98
Nagoya	0·36	—	—	—	0·20	6·00

The results arrived at may be summarised as follows. It is very probable that the two carbides, Fe_3C and WC, exist in magnet steels (compare Arnold and Read, *Proc. Inst. Mech. Eng.*, March 20th, 1914). These two carbides, according to the heat treatment, can exist either as a double carbide or as the separate carbides. If the specimen is heated once to 800—900° and then slowly cooled, the double carbide is formed; above the Ac_1 point the double carbide decomposes into its components, each of which dissolves in the austenite and remains as carbide up to about 900°. On heating still further, the tungsten carbide begins to dissociate, the degree of dissociation becoming almost complete at about 1100°. The carbon and tungsten formed by dissociation remain dissolved in the austenite, the carbon giving iron cementite in solid solution.

When the specimen is cooled at a normal rate from a temperature higher than 1100°, the A_1, A_2, and A_3 transformations are brought down to a much lower temperature than the A_1 point by the retarding effect of the tungsten dissolved in austenite. At about 550° the retarded A_3 transformation commences and the ferrite holding tungsten in solution separates; this separation continues over a range of about 50°, until the concentration of the solution reaches such a value that the eutectic A_1 transformation becomes possible, this taking place somewhat abruptly at about 500°, iron cementite being set free.

If the maximum temperature exceeds 1100° it is very difficult to make the two carbides combine during slow cooling; if, however, the specimen is once cooled to the ordinary temperature and then reheated to 800—900°, recombination of the two carbides takes place on cooling.

If a specimen previously heated to 1100° is kept at 700° for a sufficiently long time, the dissolved tungsten gradually takes carbon from the iron cementite to give tungsten cementite, and the A_1 transformation takes place at this temperature, showing that the effect of the tungsten is to retard the transformation. T. S. P.

Recovery of Ammonium Molybdate from the Filtrates obtained in the Estimation of Phosphorus in Steel and Pig Iron. Richard Friedrich (*Chem. Zeit.*, 1917, **41**, 674).—After the filtrates have been concentrated and the phosphoric acid separated as ammonium magnesium phosphate, the strongly ammoniacal liquid is treated with hydrochloric acid, added drop by drop with constant stirring, until a crystalline precipitate is no longer formed.

The precipitate of ammonium molybdate is collected after a few hours, washed with a small quantity of water, and dried between sheets of filter-paper. W. P. S.

The Chlorides and Chloro-salts of Iridium. MARCEL DELÉPINE (*Ann. Chim.*, 1917, [ix], 7, 277—339).—A résumé of work already published (compare A., 1908, ii, 702, 765; 1910, ii, 34; 1911, ii, 806; 1914, ii, 209, 461). W. G.

Mineralogical Chemistry.

The Relations in Composition of the Different Forms of Natural Bitumens. CHARLES F. MABERY (*J. Amer. Chem. Soc.*, 1917, **39**, 2015—2027).—On distillation in a vacuum, Deerfield coal gave, in addition to gaseous products, tar, and an ammoniacal aqueous liquor, an oil which on distillation yielded fractions agreeing with the composition $C_{12}H_{24}$, $C_{10}H_{20}$, $C_{16}H_{28}$, $C_{17}H_{30}$, $C_{18}H_{32}$, $C_{20}H_{36}$, and a crystalline solid, $C_{30}H_{62}$, m. p. 60°; the composition of the fractions of general formula C_nH_{2n-4} resembles that of a large proportion of the constituents of the adjacent Mahone petroleum, and the suggestion is made that the coal represents an intermediate stage of decomposition between vegetable matter and the petroleum.

The asphaltic substance gilsonite, of Utah, on distillation gave members of the series C_nH_{2n} and C_nH_{2n-2}, resembling the same classes of hydrocarbon in petroleum; there were also obtained other unsaturated hydrocarbons, and nitrogenous organic compounds similar to those found in petroleum; these results are regarded as proof of the common origin of gilsonite and petroleum. Grahamite gave similar results to gilsonite, but the proportion of nitrogen compounds was lower, and hardly accords with the view that grahamite has been formed by the further modification of gilsonite.
D. F. T.

Glauconite or Greensand. EDWARD HART (*J. Amer. Chem. Soc.*, 1917, **39**, 1919).—Grains of marl from Mallica Hill and Sewell, New Jersey, were found to consist of a core of nearly pure silica and a covering layer of glauconite containing little or no silica. The glauconite contains Fe_2O_3, 41%; FeO, 3%; Al_2O_3, 18%; CaO, 2%; MgO, 5%; K_2O, 17%; Na_2O, 0·5%; and H_2O, 13·5%.
H. M. D.

Pisanite from Lading, Carinthia. H. LEITMEIER (*Centr. Min.*, 1917, 321—331).—The crystalline material occurs as a blue crust (anal. I) overlain by a green crust (anal. II) on limonite from a deposit of pyrites and copper-pyrites at Lading, near St. Michael, in the Lavant valley. Apart from a small excess of water, owing to alteration, both analyses agree with the formula

$$(Cu,Fe)SO_4,7H_2O.$$

In I the ratio of copper sulphate to iron sulphate is 45 : 55, and in II it is 31 : 69.

	CuO.	FeO.	NiO.	SO_3.	H_2O.	Total.	Insol. deducted.	Sp. gr.
I.	11·67	13·43	—	28·18	46·72	100·00	1·49	1·950
II.	8·21	17·23	0·27	27·33	46·96	100·00	11·31	1·941

Published analyses of pisanite (including salvadorite) show a range in the mixed crystals of CuO 7·56—18·81 and FeO 15·85—8·51. There thus seems to be a gap at both ends of this isomorphous series; that at the iron end may be accidental, owing to lack of analyses, whilst that at the copper end is smaller than determined experimentally by Retgers (A., 1895, ii, 160). From the above density determinations and Retgers's value 1·899 for $FeSO_4,7H_2O$ (melanterite), the value 2·02 is calculated for $CuSO_4,7H_2O$, as opposed to 2·1 given by Schaller (A., 1903, ii, 490) for the natural boothite. L. J. S.

Occurrence of Euxenite in South Sherbrooke Township, Ontario. WILLET G. MILLER and CYRIL W. KNIGHT (*Amer. J. Sci.*, 1917, [iv], **44**, 243—244).—Small masses and crystals are found in the granite pegmatite of a felspar quarry near the village of Maberley. Associated minerals are pink felspar, quartz, tourmaline, mica, and pyrites. Analysis gave:

Ta_2O_5.	Cb_2O_5.	TiO_2.	ThO_2	Ce_2O_3,La_2O_3.	Y_2O_3, etc.	Fe_2O_3.	FeO.
13·89	12·73	27·70	1·34	0·62	25·64	2·63	0·51

MnO.	PbO.	U_3O_8.	CaO.	MgO.	SiO_2.	H_2O, etc.	Total.	Sp. gr.
trace	0·20	10·50	0·09	0·12	0·74	3·00	99·71	4·99

L. J. S.

Analytical Chemistry.

Treatment of Corks used in Soxhlet and other Extraction Apparatus. T. J. WARD (*Analyst*, 1917, **42**, 326—327).—Gelatin is soaked in cold water for five hours, the unabsorbed water is then decanted, the gelatin is heated until melted, and mixed with $\frac{1}{4}$ volume of glycerol and 2 volumes of water. The corks, previously bored, are immersed in this solution and heated in the same for two hours on a water-bath; they are then removed, wiped, and dried in a warm place. Corks thus treated are impervious to the vapours of ether, light petroleum, benzene, and carbon disulphide, and do not yield any extractives to these solvents. W. P. S.

Estimation of Halogens in Organic Compounds. J. F. Lemp and H. G. Broderson (*J. Amer. Chem. Soc.*, 1917, **39**, 2069—2074).—A variety of organic chloro-, bromo-, and iodo-compounds have been analysed with respect to halogen by the Parr sulphur-bomb method (A., 1908, ii, 628; see also Pringsheim, A., 1904, ii, 146, 775), in which oxidation is effected with sodium peroxide. Correct results are obtainable in this way, care, however, being necessary to ensure a thorough and uniform fusion, the addition of an excess of silver nitrate to the alkaline solution obtained after the oxidation process, and the reduction of any halogen oxy-acids that may have been formed, hydrazine hydrate being the most suitable reagent for the last purpose. D. F. T.

Estimation of Chlorine in Blood Serum and other Body Fluids. M. Laudat (*J. Pharm. Chim.*, 1917, [vii], **16**, 168—171).—Five c.c. of the serum are mixed with 10 c.c. of *N*/10-silver nitrate solution, 6 c.c. of saturated potassium permanganate solution, and 10 c.c. of concentrated nitric acid, and the mixture is heated until a clear liquid is obtained; this requires only a few minutes. The mixture is then diluted and the excess of silver nitrate is titrated with *N*/10-thiocyanate solution, using iron alum as the indicator. W. P. S.

Modification of the McLean-Van Slyke Method for the Estimation of Chlorides in Blood. G. L. Foster (*J. Biol. Chem.*, 1917, **31**, 483—485. Compare McLean and Van Slyke, A., 1915, ii, 573).—The modification consists in the precipitation of the proteins of the blood by treatment with metaphosphoric acid instead of by heat and blood charcoal. H. W. B.

Identification of Chlorates in the Presence of Hypochlorites. Fritz Wischo (*Pharm. Post.*, 1917, **50**, 381; from *Chem. Zentr.*, 1917, ii, 133).—The following behaviour of the two substances towards brucine and hydrochloric acid can be used for the identification of sodium chlorate in the presence of sodium hypochlorite in Dakin's solution. When a solution of sodium hypochlorite (5 c.c.) of approximately the same concentration as Dakin's solution (about 0·5%) is treated with brucine hydrochloride or sulphate (0·05 gram) and dilute hydrochloric acid (5 drops), a yellow coloration is developed which becomes cherry-red when the solution is boiled; the latter coloration remains unchanged when the solution is boiled with a further 10 c.c. of dilute acid. On the other hand, a similar solution of potassium chlorate is not coloured by brucine (0·05 gram) and dilute hydrochloric acid (5 drops) in the cold; when boiled, the solution becomes yellow, and, subsequently, cherry-red, but the colour is discharged when boiling is continued after a further addition of dilute hydrochloric acid (10 c.c.). This decolorisation on subsequent boiling with much dilute hydrochloric acid is characteristic of the presence of chlorate; it also occurs when 5 c.c. of a solution containing 0·04 gram of sodium hypochlorite and 0·02 gram of potassium chlorate in water (10 c.c.) is tested as described above. H. W.

Estimation of Bromides. E. Rupp (*Arch. Pharm.*, 1917, **255**, 303—304).—The bromate method of estimating the bromide in alkali bromides or their mixtures ("bromum compositum") is modified as follows to avoid the use of hydrogen peroxide (compare this vol., ii, 327). Twenty c.c. of officinal dilute sulphuric acid, 50 c.c. of $N/100$-potassium bromate, 0·2 gram of iodine, and 0·15 gram of the bromide are diluted to 200 c.c., and the mixture is boiled after the addition of a little talc or powdered pumice until the volume has been diminished to 75 c.c. in not less than forty minutes. The mixture is cooled to the ordinary temperature, 0·5—1 gram of potassium iodide is added, and the iodine liberated by the excess of the bromate is titrated with $N/10$-thiosulphate after three to five minutes.

When the bromide is being estimated in the presence of more than about 25% of chloride, the undiluted mixture of the sulphuric acid, potassium bromate, and iodine is concentrated to about half its volume by boiling for fifteen minutes, the solution of the haloid is added, the mixture diluted to 200 c.c., and the procedure mentioned above followed. The result is 0·2—0·3 c.c. too high if the preliminary boiling is omitted. C. S.

Estimation of Selenium in Bones, Teeth, and Urine. Th. Gassmann (*Zeitsch. physiol. Chem.*, 1917, **100**, 182—189. Compare A., 1916, i, 772).—The bones are extracted with ether, powdered, and dried at 110° to 120°, and then a weighed quantity dissolved in hydrochloric acid. After diluting with an equal volume of water, a brown precipitate containing the selenium gradually settles out. It is collected, treated with hot aqua regia, filtered, and the selenium in the filtrate precipitated as sulphide. The sulphide is then dissolved in fuming nitric acid, and silver nitrate added. The silver–selenium compound is ignited in a crucible, the residue extracted with nitric acid, and the selenium finally thrown out as a reddish-brown precipitate by dilution with water. It is collected and dried at 100°.

Healthy teeth contain about 0·056% of selenium, and even in the diseased condition about the same figures for the selenium content are obtained. The urine contains 0·0011% of selenium in the male and 0·0009% in the female person. Most vegetables contain traces of selenium, especially spinach. H. W. B.

Micro-Kjeldahl Methods. Emil Abderhalden and Andor Fodor (*Zeitsch. physiol. Chem.*, 1917, **100**, 190—201).—A detailed description of the Kjeldahl method applied to the estimation of nitrogen in small amounts of materials, such as 0·5 c.c. of urine or 10 mg. of an amino-acid. H. W. B.

Estimation of Phosphorus in Cast Iron. Alfredo Cavazzi (*Ann. Chim. applicata*, 1917, **8**, 1—6).—The author modifies the usual process by dissolving the iron in nitric acid and then converting the ferric nitrate, not into oxide and subsequently chloride, but into ferric sulphate, from the solution of which ammonium phosphomolybdate is precipitated in the usual way. In the process described, the ferric sulphate is not heated above 210°, and this is quite safe, as it does not decompose at 350°. R. V. S.

A Simplified Micro-combustion Method for the Estimation of Carbon and Hydrogen. LOUIS ELSBERG WISE (*J. Amer. Chem. Soc.*, 1917, **39**, 2055—2068).—A description of a modification of the Pregl method of micro-analysis of organic substances. The quantity of substance taken is 11—22 mg., and is weighed on an accurate analytical balance of the ordinary type instead of on a micro-balance. For the modifications suggested in the carbon dioxide absorption tube, in the drying train, and in the method of operating, the original should be consulted. D. F. T.

Microchemical Analysis of Explosive Substances. G. KARL ALMSTRÖM (*J. pr. Chem.*, 1917, [ii], **95**, 257—260).—Pregl's method of micro-analysis can be extended to explosive substances if the weighed quantity of the substance under examination is mixed with sand; under such conditions, the combustion can proceed quietly and yield accurate results. Details of the procedure are given, together with the results of analyses of diazobenzenesulphonic acid, silver acetylide, and potassium picrate. In the case of salts of the alkali metals, in order to prevent the formation of a residue of alkali carbonate, it is necessary to mix with lead chromate instead of with sand. D. F. T.

Estimation of Organic Carbon in Water. ATILIO A. BADO (*Anal. Soc. Quim. Argentina*, 1917, **5**, 102—106).—An account of a modification of the Carrasco-Plancher method for estimating organic carbon in sewage and natural waters. It is recommended as both accurate and rapid. A. J. W.

Source of Error in the Analysis of Generator Gas. ALFRED KROPF (*Zeitsch. angew. Chem.*, 1917, **30**, i, 177—179).—The absorption of carbon monoxide by cuprous chloride solution presents certain difficulties and is usually incomplete; the whole of this gas may, however, be absorbed if three absorption vessels are used, the first two containing cuprous chloride solution acidified with hydrochloric acid, and the third ammoniacal cuprous chloride solution. The quantity of nitric oxides formed during the combustion of the residual gases in the explosion pipette may be calculated from the observed contraction, quantity of oxygen used, etc. W. P. S.

Automatic Estimation of Carbon Dioxide (Carbonates) in Soils. Classification of Soils. G. HUTIN (*Ann. Chim. anal.*, 1917, **22**, 158—160).—In the apparatus described the soil is treated with hydrochloric acid in a flask connected with a chamber provided with a mercury manometer; a float is actuated by the difference in pressure due to the liberation of the carbon dioxide from the soil, and the movements of the float are marked in the usual way on a mechanical recorder. The graph obtained shows whether the carbon dioxide is evolved slowly or quickly from the carbonates in the soils, and thus affords an indication of the kind of carbonate present. W. P. S.

Estimation of Potassium and Sodium in Vegetable Ashes. H. PELLET (*Ann. Chim. anal.*, 1917, **22**, 146—152, 179—185).—The ash is obtained by incinerating the vegetable substance at a relatively low temperature, extracting the carbonised mass with water, igniting the insoluble portion separately, adding this ash to the aqueous solution, and evaporating the latter to dryness; the dry residue is then ignited. In some cases it is necessary to make two extractions with water in order that the carbonised mass may be burnt readily to a white ash. Five grams of the ash are extracted repeatedly with boiling water, the extracts are filtered, and diluted to 500 c.c.; 200 c.c. of this solution are treated with an excess of barium hydroxide solution, the excess of barium hydroxide is converted into carbonate by means of carbon dioxide or ammonium carbonate, and, after filtration, the solution is evaporated with the addition of hydrochloric acid, and the residue of alkali chlorides is ignited and weighed. The potassium in the mixed chlorides is estimated by means of platinum chloride, and the amount of sodium is found by difference. If desired, the potassium platinichloride may be reduced by heating with sodium formate and the reduced platinum collected and weighed. The filtrate and washings from the potassium precipitate may be evaporated to expel ether and alcohol, and the platinum separated by reduction with ammonium formate; the filtrate from the platinum precipitate is evaporated, the residue ignited to expel ammonium salts, then evaporated with the addition of hydrochloric acid, and the residue of sodium chloride weighed. W. P. S.

Estimation of Silver in Organic Compounds. H. J. LUCAS and A. R. KEMP (*J. Amer. Chem. Soc.*, 1917, **39**, 2074—2078).—For the estimation of silver in an organic silver salt, especially of such acids as contain sulphur, it is recommended that a slight excess of $N/4$-sodium cyanide solution be added to 0·3 gram of the substance, and then, after the addition of 10 c.c. of N-sodium hydroxide and dilution to 300 c.c., the silver be precipitated as sulphide by the addition of 25 c.c. of $N/4$-sodium sulphide; physico-chemical reasons are given for the proportions of the reagents. The advantages claimed include accuracy, speed, and the possibility of recovering the organic acid. D. F. T.

The Blacher Method for the Estimation of Hardness in Water. A. S. BEHRMAN (*Philippine J. Sci.*, 1916, **11**, [*A*], 291—293).—The presence of large quantities of free carbon dioxide renders the estimation of temporary hardness (titration with sodium

carbonate solution) untrustworthy; aspiration for five minutes will reduce the quantity of free carbon dioxide to below 28 parts per million of water, an amount which has no effect on the titration. Sodium chloride, even when present in large amount, does not interfere. In the titration of the total hardness (with potassium palmitate, using phenolphthalein as indicator) the end-point is denoted by the appearance of a light red coloration; the very faint red coloration which first appears should be ignored. This applies particularly to waters containing magnesium salts in addition to calcium salts.
W. P. S.

The Estimation of Copper as Sulphide and by Electrolysis. FRIEDRICH L. HAHN (*Zeitsch. anorg. Chem.*, 1917, **99**, 201—248).—It is not possible to obtain pure cuprous sulphide by heating cupric sulphide in hydrogen, as the temperature at which the second atom of sulphur is completely driven off in a reasonable time is very close to that at which reduction to metallic copper takes place. Heating in carbon dioxide in a Rose crucible gives variable results. Many experiments with different kinds of tubes are described, the precipitates being heated in various atmospheres and at known temperatures. If air enters the tube or crucible, oxygen is always absorbed in time, even at moderate temperatures, sulphate being formed with increase of weight. At high temperatures oxygen causes a loss of weight, owing to the formation of cuprous oxide or metallic copper.

Two methods have been found to give satisfactory results. One consists in heating the sulphide in a mixture of hydrogen sulphide and hydrogen, the proportions of which may vary within wide limits. A glazed Rose crucible is used, heating strongly over a Méker burner or blowpipe. During the first part of the heating the gas used is chiefly hydrogen sulphide, and towards the end chiefly hydrogen, separate bubbling tubes being used for the two gases. Two minutes suffice for 0·2 gram of sulphide, ten minutes for larger quantities. The weight becomes quite constant, and the precipitate, being highly crystalline, is not hygroscopic.

Ignition at first in hydrogen sulphide and then in carbon dioxide saturated with methyl alcohol also gives good results.

Copper may be estimated electrolytically in nitric acid solution. When pure platinum electrodes are used, platinum is dissolved at the anode, but platinum–iridium anodes are not attacked. Stationary gauze cathodes or rotating apparatus may be used, and the trace of copper remaining in solution is estimated colorimetrically.
C. H. D.

Detection of Mercury for Forensic Purposes. CARLO LUIGI SPICA (*Boll. chim. farm.*, 1917, **56**, 437—440; *Gazzetta*, 1917, **47**, ii, 139—144).—In cases of suspected mercurial poisoning, it is of importance to be able to decide whether the mercury found *post-mortem* was in the form of a soluble or insoluble compound when ingested. From his experiments on viscera preserved in aqueous alcohol, the author finds that mercuric chloride passes in time into a compound, from which it can be extracted only by the use of hydrochloric acid. When calomel is kept in like manner in contact with visceral material for a long time, it is very doubtful whether any of it is converted into a compound soluble in aqueous alcohol, but a considerable quantity of it is found in a form soluble in hydrochloric acid, and much of it remains apparently unchanged.

R. V. S.

Separation and Detection of Gallium. PHILIP E. BROWNING and LYMAN E. PORTER (*Amer. J. Sci.*, 1917, **44**, 221—224).—Gallium is readily separated, together with glucinum and aluminium, from the other elements by the usual methods; glucinum rarely occurs in products containing gallium, so the latter has only to be separated from aluminium. In a strong hydrochloric acid solution, as little as 0·0002 gram of gallium yields a precipitate with potassium ferrocyanide, but aluminium gives no precipitate. The gallium ferrocyanide may be collected, fused with ammonium nitrate, the iron precipitated with an excess of sodium hydroxide, and the gallium then recovered as hydroxide by heating the filtrate with the addition of ammonium chloride. Traces of zinc may remain in the solution containing the gallium and aluminium and interfere with the ferrocyanide reaction; these traces may be removed by treating the strongly alkaline solution with hydrogen sulphide. Nitrates, or nitric acid, must be removed by evaporation with hydrochloric acid before the ferrocyanide test is applied.

W. P. S.

Analysis of Alloys of Nickel and Zirconium. G. L. KELLEY and F. B. MYERS (*J. Ind. Eng. Chem.*, 1917, **9**, 854).—The following method may be used for the analysis of alloys having the approximate composition: carbon, 0·1 to 0·5%; nickel, 70·0 to 90·0%; iron, 2·0 to 6·0%; silicon, 2·0 to 8·0%; aluminium, 0·5 to 10·0%; zirconium, 2·0 to 18·0%; tungsten, 0·5 to 10%; and manganese, 0·1 to 0·3%. The alloy is dissolved in aqua regia and the solution is evaporated with the addition of sulphuric acid; after dilution, the silica and tungstic oxide are separated by filtration, ignited, and weighed. The silica is then expelled by evaporation with hydrofluoric acid, and the residue of tungstic oxide is weighed. To remove remaining traces of iron, aluminium, and zirconium, this residue is fused with sodium carbonate, the mass treated with water, filtered, the insoluble portion weighed, and the weight deducted from that of the tungstic oxide; the insoluble portion is now fused with potassium hydrogen sulphate, dissolved in water, precipitated with ammonia, and the precipitate then redissolved in hydrochloric acid. The combined solutions from the silica and tungstic oxide are diluted to a definite volume; a portion of this solution is heated, treated with ammonia, the precipitate collected, dissolved in dilute sulphuric acid, and the iron is reduced and then titrated with permanganate solution. To another portion of the solution ammonia is added in excess and the nickel is deposited electrolytically. The solution is then boiled to expel most of the ammonia, the precipitated hydroxides are collected, dissolved in hydrochloric acid, and the aluminium is separated by treating the solution with an excess of potassium hydroxide. The ferric and zirconium hydroxides are dissolved, reprecipitated with ammonia, collected, ignited, and weighed; the quantity of iron is found by titration and that of the zirconium by difference. If manganese is present, a further portion of the solution is boiled with the addition of ammonia and ammonium persulphate, the precipitate formed is collected, dissolved in nitric acid with the addition of a small quantity of hydrogen peroxide, the manganese is oxidised with sodium bismuthate, and estimated by one of the usual methods.

W. P. S.

New Volumetric Method for the Estimation of Molybdenum and Vanadium in Steels. TRAVERS (*Compt. rend.*, 1917, **165**, 362—364).—For the estimation of molybdenum the steel is attacked with concentrated hydrochloric acid or by 5% sulphuric acid, potassium permanganate, in just sufficient amount, being used to oxidise the iron, which is then precipitated by pouring the liquid into an excess of boiling aqueous potassium hydroxide. An aliquot portion of the filtrate from this is acidified with hydrochloric acid, so that the liquid contains 1 c.c. of free hydrochloric acid in each 100 c.c. This solution, when cool, is reduced with an excess of titanous chloride, which is titrated back with ferric chloride solution, using potassium thiocyanate as indicator. For concentrations of molybdenum less than 0·05 gram per litre, and under the above conditions, the reduction proceeds according to the equation $2MoO_3 = Mo_2O_5 + O$. Vanadium may be estimated in a similar manner, the reduction being $V_2O_5 = V_2O_4 + O$. If both molybdenum and vanadium are present in the steel, the two are estimated together; the vanadium is then estimated colorimetrically by means of hydrogen peroxide, and the molybdenum obtained by difference. If tungsten is present, it must be eliminated by precipitation prior to the above estimations. W. G.

Estimation of Tungstic Acid in Wolframite. LUIS GUGLIALMELLI and ULAUS HORDH (*Anal. Soc. Quim. Argentina*, 1917, **5**, 81—90).—The authors point out that there is a liability to error in the ordinary methods of estimating tungsten in wolframite, owing to the formation of complex silicotungstic acids.

A. J. W.

A New Separation of Tin and Tungsten in Stanniferous Wolframs. TRAVERS (*Compt. rend.*, 1917, **165**, 408—410).—The finely powdered mineral is fused with anhydrous sodium sulphide, and the mass, when cold, is broken up with boiling water, diluted to 800 c.c., and feebly acidified. The stannous sulphide is filtered off, along with a little silica and sulphides of iron and manganese, and is purified by solution in ammonium sulphide, containing sulphur. It is reprecipitated by acid and ignited to stannic oxide.

For the estimation of the tungsten, a further portion is fused as above, and the mass dissolved in aqua regia, the solution being evaporated to dryness and the residue taken up with hydrochloric acid. The insoluble residue consists of most of the tungsten in the form of its oxide and some silica. To the filtrate ammonium hydroxide is added in just sufficient amount to precipitate the iron. This precipitate is filtered, washed free from sodium salts, and dissolved on the filter in hot 50% hydrochloric acid. The solution is evaporated to dryness and taken up with hydrochloric acid, the tungsten being left as its oxide. Any silica present in the two tungsten precipitates is separated by the ordinary processes. W. G.

Detection of Germanium and its Separation from Arsenic. Philip E. Browning and Sewell E. Scott (*Amer. J. Sci.*, 1917, [iv], **44**, 313—315).—The substance, for example, zinc oxide, supposed to contain germanium, is distilled with concentrated hydrochloric acid to which a small quantity of potassium permanganate has been added (compare Buchanan, A., 1916, ii, 486), and the distillate is collected in water contained in a well-cooled receiver. The distillate is then treated with hydrogen sulphide; a white precipitate forms if as little as 0·0001 gram of germanium is present. The potassium permanganate is added to provide the chlorine necessary to prevent reduction of arsenic sulphide and distillation of arsenic; a trace of chlorine may pass into the distillate and produce a cloudiness with hydrogen sulphide, but a precipitate does not form unless germanium is present.

If, as proposed by Winkler (A., 1887, 1081), the mineral is fused with sodium carbonate and sulphur, the mass dissolved in water, the solution treated with ammonium acetate, acidified with acetic acid, and then treated with hydrogen sulphide, any arsenic present is precipitated completely, whilst germanium remains in solution.

W. P. S.

Estimation of Tantalum in Alloy Steels. G. L. Kelley, F. B. Myers, and C. B. Illingworth (*J. Ind. Eng. Chem.*, 1917, **9**, 852—854).—The alloy is dissolved in dilute hydrochloric acid, the solution evaporated to dryness, the residue boiled with hydrochloric acid, and collected on a filter. The filtrate is evaporated to a small volume with the addition of nitric acid, 50 c.c. of concentrated hydrochloric acid are added, the mixture is evaporated to a syrup, and the ferric chloride extracted with ether. The aqueous solution is now heated to expel dissolved ether, evaporated with sulphuric acid, diluted, boiled with the addition of silver nitrate and ammonium persulphate, and then rendered ammoniacal. The precipitate formed contains all of the soluble tantalum and aluminium with traces of chromium, vanadium, and manganese; it is collected, added to the insoluble residue of the first filtration, ignited, and fused with potassium hydrogen sulphate. The mass is treated with hot dilute hydrochloric acid, the insoluble residue of silica and tantalum oxide is collected, ignited, and the silica is removed by treatment with hydrofluoric acid. If the alloy contains tungsten, it is treated in the first place with a mixture of dilute hydrochloric and nitric acids, the insoluble tungstic oxide is separated, treated with ammonia, and the residue thus obtained is combined with the precipitate obtained at a later stage of the process as described above; the residue of silica and tantalum oxide should, however, be treated with dilute ammonia to remove remaining traces of tungstic oxide. W. P. S.

Modification of the Nicloux Method for Estimating Ethyl Alcohol. E. M. P. Widmark (*Skand. Arch. Physiol.*, 1916, **35**, 125—130). **Some Measurements of the Alcohol Content of the Urine in Intoxicated Persons.** E. M. P. Widmark (*Hygiea*, 1917, **79**, 158—168; from *Physiol. Abstr.*, 1917, **2**, 342—343).—Five c.c. of urine are boiled for one and a-half minutes with a little kaolin over a free flame, and the distillate is received into a mixture of 5 c.c. of concentrated sulphuric acid and 2 c.c. of 2·3% potassium dichromate, the latter amount being almost reduced by 10 mg. of alcohol. By titration with standard alcohol (0·5% by weight) the tint of the control is matched; the latter is freshly prepared by distilling 10 mg. of alcohol into a similar dichromate mixture. For amounts of alcohol lower than 5 c.c. the amount of dichromate must be halved. Four series of ten determinations with 1·2—7·5 mg. gave results 4·4—0·1% too low. The highest value in urine among twenty-seven cases was 5·7%, much higher than the figures obtained for the blood with Nicloux's method by Schweisheimer. Compare also Pringsheim (A., 1908, ii, 767), who has given a useful method for estimating alcohol in blood. G. B.

Estimation of Glycerol, Crude Glycerol, and Glycerol Lyes. K. Löfel (*Zeitsch. angew. Chem.*, 1917, **30**, i, 197—200).—A brief description of the methods which have been described; these include physical methods (distillation, refraction, specific gravity, vapour pressure, etc.), oxidation methods (with permanganate or dichromate), esterification methods (benzoate, acetin, iodide), and various other methods, such as those in which the glycerol is weighed as glyceryl nitrate or sodium glycerate.
W. P. S.

Identification of the Naphthols. A New and Delicate Test for α-Naphthol. Luis Guglialmelli (*Anal. Soc. Quim. Argentina*, 1917, **5**, 97—101).—α-Naphthol gives an intense blue coloration with sodium arsenotungstate, but the β-isomeride gives no coloration with this reagent. A. J. W.

Convenient Filtration Apparatus for the Estimation of Sugar by Titration of the Cuprous Oxide Precipitated from Fehling's Solution. F. Boericke (*Zeitsch. angew. Chem.*, 1917, **30**, i, 24).—An Allihn filter tube for the estimation of sugar is fused into a bulb blown on the end of a short piece of glass tubing which fits, with a ground-glass joint, either into a filter flask or a conical flask. A narrow piece of glass tubing, fitted with a tap, is also fused into the side of the bulb.

The apparatus may be used in either of the following ways. (1) It is fitted into the filter flask, whilst the conical flask is used for the precipitation of the cuprous oxide from Fehling's solution and the sugar. The liquid is then decanted from the cuprous oxide through the filter tube, as also the washings from the cuprous oxide. The rate of filtration in the apparatus can be controlled by manipulation of the tap in the side-tube of the bulb. When decantation and washing are complete, the filter flask is replaced by the conical flask, which contains the main portion of the cuprous oxide. By applying suction to the side-tube, hot ferrous sulphate solution may then be run through the Allihn tube to dissolve the cuprous oxide, and the estimation carried out in the usual way.

(2) The apparatus is fitted into the conical flask, into which filtration takes place directly. The amount of unreduced Fehling's solution in the filtrate is then estimated. T. S. P.

Estimation of Dextrose in Blood. BAUZIL and BOYER (*J. Pharm. Chim.*, 1917, [vii], **16**, 171—179).—The blood is clarified by heating with 25% sodium sulphate solution containing a small quantity of acetic acid and then filtering the mixture. An alternative method consists in shaking the blood with alcohol, filtering the mixture, evaporating the filtrate to expel alcohol, and then treating the liquid with sodium sulphate solution and acetic acid. The dextrose is estimated by Fehling's solution; instead of weighing the cuprous oxide, the excess of copper in the filtrate is titrated with potassium cyanide solution after the addition of ammonia, or the blue solution may be treated with ammonia, a definite volume of standardised potassium cyanide solution, and a small quantity of potassium iodide, and then titrated with *N*/10-silver nitrate solution. W. P. S.

Estimation of the Dextrose in the Blood in Reference to the Condition in which it is Present. HUGH MCGUIGAN and E. L. ROSS (*J. Biol. Chem.*, 1917, **31**, 533—547).—Higher figures for the dextrose in the blood are obtained by the Benedict method than by that of Bertrand when the Fehling's solution employed contains 12·5% of potassium hydroxide. When the strength of the alkali is reduced to 5%, both methods give the same result. It is thought that the difference obtained in the first case is due to the presence of an unknown organic interfering substance which prevents the precipitation of the cuprous oxide. H. W. B.

Estimation of Sugar in Urine. D. SIDERSKY (*Ann. Chim. anal.*, 1917, **22**, 170).—In the volumetric estimation of reducing sugars with Fehling's solution, the addition of magnesium sulphate (5 grams per 500 c.c. of the copper sulphate solution) causes the cuprous oxide to settle rapidly during the titration. W. P. S.

Volumetric Estimation of Sugar in Urine with Fehling's Solution. Ruoss (*Zeitsch. anal. Chem.*, 1917, **56**, 369—384).—The use of the following reagents is recommended: Copper sulphate solution containing 6·9278 grams of copper sulphate and 25 grams of sodium chloride per 100 c.c. Alkaline tartrate solution containing 34·6 grams of potassium sodium tartrate, 10·3 grams of sodium hydroxide, 3 grams of potassium thiocyanate, and 5 grams of sodium chloride per 100 c.c. The end-point of the titration is ascertained by adding 5 c.c. of dilute acetic acid containing 10% of sodium chloride to the hot mixture, followed by 3 drops of 5% potassium ferrocyanide solution; a brown coloration indicates the presence of cupric salts, and the titration must, in this case, be repeated, using a larger volume of the sugar solution. Attention is directed to the fact that urine free from sugar reduces Fehling's solution to an extent which may in some cases be equivalent to the presence of 0·2% of reducing sugar. W. P. S.

The Possibilities and Limitations of the Duclaux Method for the Estimation of Volatile Acids. L. J. Gillespie and E. H. Walters (*J. Amer. Chem. Soc.*, 1917, **39**, 2027—2055).—A review and examination of the method of Duclaux (this Journ., 1875, 188) for the investigation of a mixture of volatile fatty acids in aqueous solution by the behaviour on distillation. Algebraic and graphic methods for the computation of the results for mixtures of two or three acids are described, and the algebraic calculation for four or more acids is indicated. Application of the method to known mixtures shows that with two or three acids present, a quantitative analysis may be made without very great error; if the method is to be applied to mixtures of more than three acids, the mixture must first be resolved by fractionation into portions containing only three acids. D. F. T.

Estimation of Salicylic Acid in Foods. H. D. Steenbergen (*Chem. Weekblad*, 1917, **14**, 914—921).—An investigation of various methods of estimating salicylic acid in foods. A. J. W.

A very Delicate Reaction of the Nitriles. S. Dezani (*Atti R. Accad. Sci. Torino*, 1917, **52**, 826—833).—When a solution of a nitrile (aliphatic or aromatic) is treated with an equal volume of hydrogen peroxide (12 vols. %) and 2—3 drops of a 5% solution of ferric chloride, hydrogen cyanide is produced on boiling. This can be detected by test papers made by treating filter-paper with picric acid (1%), drying, and then immersing the paper in a 10% solution of sodium carbonate. If much nitrile is present, the paper turns blue, but with smaller quantities a red or brownish-red coloration is observed. Very small quantities of nitrile can be detected in this way, the limit being about 2×10^{-5} gram of HCN. The reaction is applied to the detection of nitriles in urine. R. V. S.

Cryoscopy and Refractometry of Milk. J. Pritzker (*Zeitsch. Nahr. Genussm.*, 1917, **34**, 69—112).—It is now established that the freezing point of milk varies but very little from $-0.55°$, and that it is not affected by the breed, age, feeding, or time of milking of the cows. It is influenced, however, by the acidity of the milk and by the presence of preservatives; each degree of acidity (Soxhlet-Henkel scale) decreases the freezing point by about 0·008°, and the addition of 0·1% of formaldehyde decreases it by 0·03°. Potassium dichromate raises the freezing point. The use of calcium chloride in the preparation of milk serum has an influence on the freezing point and refractometer number of the serum according to the quantity of calcium chloride added; the freezing point of the serum is lower than the sum of the freezing points of the milk and the added quantity of calcium chloride solution. The freezing point of milk varies correspondingly with the refractometer number.

W. P. S.

Application of the Cryoscopic Method for Estimating Added Water in Milk. J. T. Keister (*J. Ind. Eng. Chem.*, 1917, **9**, 862—865).—The freezing point of milk ($-0.54°$ to $-0.57°$) affords the most trustworthy basis on which to draw conclusions as to the presence or absence of added water in milk. In the greater number of cases the presence of as little as 5% of added water can be detected by the method. It is essential that the process be applied only to fresh milk, since the freezing point is lowered by about 0·003° for each 0·01% increase of acidity. The presence of formaldehyde lowers the freezing point. The method may be used in milk-control work, as it need be applied only to samples of doubtful character.

W. P. S.

Braun's Reagent. I. J. Rinkes (*Chem. Weekblad*, 1917, **14**, 895—896. Compare Braun, A., 1908, i, 700).—An account of the application of Braun's reagent to the detection of aldehydes, and to the distinguishing of ketoaldehydes and dialdehydes.

A. J. W.

Estimation of the Acetone Substances in Urine, together with an Altered Procedure for a Separate Estimation of Acetone and Acetoacetic Acid in Urine. N. O. Engfeldt (*Zeitsch. physiol. Chem.*, 1917, **100**, 93—110).—The author, finding that the method for the separate estimation of acetone and acetoacetic acid in urine described by Lenk (this vol., ii, 399) is not satisfactory, proposes the following modification, which furnishes nearly accurate results. One hundred c.c. of 5% potassium permanganate are diluted with 100 c.c. of water and acidified with 1 c.c. of acetic acid. To this, 10 c.c. of urine are added, and the mixture distilled for twenty minutes into 100 c.c. of water. The distillate is diluted to about 300 c.c., 20 c.c. of 25% sodium hydroxide and 10 c.c. of 3% hydrogen peroxide are added, and the mixture again distilled for thirty-five to fifty minutes. The acetone in the second distillate is estimated by the Messinger method, and constitutes the acetone preformed in the urine. The total acetone plus acetoacetic acid is estimated in the usual way by the Messinger method, and the difference between the two results represents the acetoacetic acid, calculated as acetone, in the original urine. The result obtained is stated to be about 5% less than that actually present.

From 80% to 90% of the total acetone in a fresh urine is usually present in the form of acetoacetic acid. H. W. B.

Estimation of Ferricyanides by Titration with Permanganate. C. DE COQUET (*Bull. Soc. Pharm. Bordeaux*, 1917; from *Ann. Chim. anal.*, 1917, **22**, 160—161).—The solution, containing about 0·25 gram of ferricyanide, is gently heated with the addition of 0·5 gram of aluminium and 25 drops of sodium hydroxide solution; the reduction of the ferricyanide requires about twenty minutes. The mixture is then diluted, filtered, the filtrate acidified with sulphuric acid, and titrated with *N*/10-potassium permanganate solution; each c.c. of the latter solution is equivalent to 0·033 gram of potassium ferricyanide. When the quantity of ferricyanide present is less than 0·5 gram, 0·2 c.c. is deducted from the volume of permanganate solution used. The method may be employed for the estimation of ferricyanide in certain photographic powders, which also contain uranium nitrate, ammonium iron citrate, and copper chloride. The powder is dissolved in water, the solution rendered alkaline with sodium hydroxide, diluted to 50 c.c., filtered, and 25 c.c. of the filtrate are taken for the estimation as described. W. P. S.

Effect of Temperature on the Reaction of Lysine with Nitrous Acid. BARNETT SURE and E. B. HART (*J. Biol. Chem.*, 1917, **31**, 527—532).—By raising the temperature, the reaction between lysine and nitrous acid is accelerated, and, above 30°, all the nitrogen is expelled in ten minutes. It is sufficient, therefore, if the temperature is raised to 30° or over, to shake the hexone bases in the Van Slyke method of protein analysis for fifteen minutes instead of for thirty minutes, as usually recommended. At temperatures of 1° and under, the ε-amino-group of lysine does not react with nitrous acid. H. W. B.

Identification of the Poisons Extractable from Acid Aqueous Solution by Means of Ether according to the Stas-Otto Process (Veronal, Acetanilide, Salicylic Acid, Phenacetin). O. TUNMANN (*Apoth. Zeit.*, 1917, **32**, 289—292, 298—299; from *Chem. Zentr.*, 1917, ii, 137—139).—The microchemical identification of the above-mentioned substances is effected as follows. *Veronal.*—Zinc chloroiodide solution is added to the sublimate from the veronal residue beneath a cover slip; numerous, generally small (up to 40 μ long and 20 μ wide), flat, tabular, and prismatic crystals are immediately formed, which vary in colour from pale grey to blackish-red. They are optically biaxial, have extraction parallel to the long axis, are rhombic, and show strong pleochroism (colourless to blackish-red). The crystals are stable. Acetanilide and salicylic acid do not react with zinc chloroiodide. The veronal sublimate is dissolved by hydriodic acid, and crystals are slowly deposited at the edges of the solution; these are relatively large (up to 150 μ long and 50 μ wide), flat, red, or sometimes grey, optically biaxial, have direct extinction, and shine red between crossed Nicols. With bromine-potassium bromide solution, a red colour is developed, due to a mixture of flesh-coloured and red needles and leaflets, which polarise strongly and show direct extinction and very marked pleochroism. They attain a length of 50—80 μ, whilst, also, very small groups of yellow crystals are formed. The red crystals disappear in course of time, whilst the yellow are more stable. If the veronal sublimate is dissolved in ammoniacal copper solution and the latter allowed to evaporate, a mixture of pink to violet lamellæ and coarse plates is obtained, which shines in polarised light. The plates belong to the monoclinic system, are optically biaxial, and have oblique extinction.

Acetanilide.—Well-formed crystals are obtained by sublimation and recrystallisation from water. With hydriodic acid, reddish-brown drops are formed immediately, from which crystals of iodoacetanilide separate after a few minutes. These are strongly dichroic (reddish-brown and pale yellow), and show extinction parallel to the long axis. They are stable. Bromoacetanilide is prepared by the addition of bromine-potassium bromide solution to the sublimate dissolved in hot water; a yellow solution results, from which, on addition of water, colourless crystals separate. These consist of fine needles, which are transformed partly into prismatic aggregates and partly into small, monoclinic crystals. The *iso*nitrile test, the identification of aniline after hydrolysis, and certain colour reactions can also be performed.

Salicylic Acid.—Sublimation can be effected without decomposition of the acid into carbon dioxide and phenol. Better crystals are obtained after solution of the sublimate in water. They consist of prismatic rodlets and coarse, generally rectangular prisms, which belong to the monoclinic system, polarise in all colours, and have oblique extinction. The sublimate was tested with iron chloride, nitric acid, and Millon's reagent, and also converted into the methyl ester (recognised by odour). If the sublimate is treated with ammonia, the solution allowed to evaporate, and silver nitrate added to the moist residue, a mixture of crystals is formed containing well-developed, oblique prisms of silver salicylate. The latter are up to 100 μ long and 15 μ wide; they polarise strongly, and have oblique extinction (monoclinic).

Phenacetin.—The sublimate should be recrystallised from water, from which the phenacetin separates in two forms. The first of these consists mainly of flat prisms with oblique ends, at which twin-formation is frequently evident; they are 15—20 μ wide and 100—150 μ long. The subsidiary form comprises very long, flat, rectangular prisms, which invariably exhibit strong, oblique grooves. The oblique and rectangular prisms have oblique and direct extinction respectively. All the crystals polarise strongly. Platelets, as with acetanilide, are not formed. Characteristic nitrophenacetin crystals are prepared by mixing the sublimate with water and nitric acid and warming without cover-glass until a yellow rim is formed.

Groups of yellow needles soon separate, which polarise strongly between crossed Nicols; slender needles, prisms, or long, flat, rectangular crystals with direct extinction are also produced. When similarly treated, salicylic acid, acetanilide, or antipyrine yield only a colourless rim and white crystals. The phenacetin sublimate does not give the carbylamine reaction. The tests with hydriodic acid and bromine–potassium bromide solution are also described.

H. W.

Improved Test for Indican in Urine. F. C. Askenstedt (*J. Lab. and Clin. Med.*, 1917, **2**, 578—580; from *Physiol. Abstr.*, 1917, **2**, 345).—The urine is diluted to D 1·005, warmed, and shaken with chloroform; Obermayer's reagent is then added, and the indigo shaken into the chloroform. If the latter remains colourless or only shows a trace of blue, the urine is normal; otherwise there is excess of indican. G. B.

A Source of Error in the Investigation of Urinary Indoxyl. Luciano P. J. Palet (*Anal. Soc. Quim. Argentina*, 1917, **5**, 93—94).—In the examination of urine for indoxyl, contradictory results are sometimes obtained by different methods. The author attributes this phenomenon to the presence of the "scatolic colours" of Porcher and Hervieux. A. J. W.

Reaction of Antipyrine with *p*-Dimethylaminobenzaldehyde. Claude Gautier (*Soc. Biol.*, 1917; from *J. Pharm. Chim.*, 1917, [vii], **16**, 189).—An orange coloration is obtained when a mixture of 10 c.c. of an aqueous antipyrine solution (containing 0·1 gram of the substance) and 1 c.c. of an alcoholic 5% *p*-dimethylaminobenzaldehyde solution is acidified with 1 c.c. of concentrated hydrochloric acid. W. P. S.

The Sensitiveness of the General Method of Extraction of Alkaloids in Water. L. Launoy (*Compt. rend.*, 1917, **165**, 360—362).—The method employed, namely, to make the water alkaline with sodium carbonate and subsequently to extract it three times with chloroform, is capable of detecting 1 part of alkaloid in two million parts of water. Two hundred c.c. of water should be extracted, the residue from the chloroform extract after evaporating off the chloroform being dissolved in 1 c.c. of 10% sulphuric acid. The acid solution is divided into two parts, one being tested with Tanret's reagent and the other with Bouchardat's reagent. W. G.

Titration and Estimation of Morphine with Iodic Acid. Jitendra Nath Rakshit (*J. Soc. Chem. Ind.*, 1917, **36**, 989—990).—The process depends on the fact that when a solution of morphine is treated with an excess of iodic acid in the presence of dilute sulphuric acid, the oxidation of the alkaloid is quantitative, two molecules of morphine absorbing three atoms of oxygen. In the estimation, morphine, either in the form of the free base, hydrochloride or sulphate (0·05—0·15 gram), is thoroughly shaken with water (50 c.c.), $N/10$-sulphuric acid (5 c.c.), and freshly prepared cooled starch solution (1%, 10 c.c.); $N/5$-iodic acid solution (5—15 c.c.) is introduced, the mixture again shaken, set aside in a dark place for about fifteen minutes, and titrated back with $N/10$-thiosulphate solution. The end-point should be taken when the blue colour has remained discharged for at least thirty seconds.

The method cannot be applied to the estimation of morphine in opium, the results obtained being too high and discordant, owing to the fact that codeine and narcotine also absorb a certain amount of oxygen under the same conditions. In addition, other substances are present in opium which likewise absorb oxygen. H. W.

Colorimetric Methods for the Estimation of very small Quantities of Morphine. A. HEIDUSCHKA and MARTIN FAUL (*Arch. Pharm.*, 1917, **255**, 172—191).—I. *Georges and Gascard's Iodic Acid Method* (A., 1906, ii, 507).—The authors employ a modification of this method. Instead of using a Duboscq colorimeter, they prepare a scale of colours by diluting a faintly acid solution of morphine in about $N/10$-hydrochloric acid to a concentration of 1 in 1000 and then preparing from this a series of solutions of concentrations down to 1 in 10,000. Equal volumes (10 c.c.) of these solutions are treated with 5 c.c. of 5% iodic acid solution, and the yellow colorations are examined after about half a minute. The differences in colour are more pronounced in the more dilute solutions. Whilst morphine can be thus detected at a concentration of 1 in 12,500, quantitative observations can only be made at concentrations between 1 in 1500 and 1 in 5500.

The method is rendered more sensitive if 1 c.c. of 10% aqueous ammonia is added about five minutes after the addition of the iodic acid. Morphine can thus be detected at a concentration of 1 in 18,500 and estimated at concentrations between 1 in 5000 and 1 in 16,500.

II. *Estimation with Marquis's Reagent.*—One c.c. of the morphine solutions prepared as above is evaporated in a small basin, the residue is treated with 1 c.c. of Marquis's reagent (2—3 drops of 40% formaldehyde solution, 3 c.c. of conc. sulphuric acid), and the violet solution is washed into the comparison tube with 4 c.c. of sulphuric acid. The colours are examined by transmitted light, since in reflected light an actual colour change from blue to bluish-brown renders the comparison untrustworthy. Morphine can thus be estimated at concentrations between 1 in 1400 and 1 in 14,000, and, the dilution with the sulphuric acid being omitted, can be detected at a concentration of 1 in 25,000.

Two samples of ripe poppy capsules examined by these methods were found to contain 0·017 and 0·068% of morphine respectively; in both cases the seeds did not contain morphine. C. S.

Detection and Presence of Carotinoids in Plants. C. VAN WISSELINGH (*Flora*, 1917, **177**, 371—432; from *Physiol. Abstr.*, 1917, **2**, 365).—The best method for obtaining crystals is by

Molisch's potassium hydroxide method; the following reagents may be used: saturated solutions of antimony trichloride and of zinc chloride in 25% hydrochloric acid, or saturated solution of anhydrous aluminium chloride in 38% hydrochloric acid. The author assumes the existence of various carotinoids; in many cases two are found in the same preparation. G. B.

Simple New Reaction for Bile Pigments. JOSEF KALLÓS (*Deut. med. Woch.*, 1917, **46**, 751; from *Chem. Zentr.*, 1917, ii, 136).—The urine (5—8 c.c.) is shaken with dilute hydrochloric acid (1—2 c.c.) and 2—3 drops of potassium or sodium nitrite (0·5%) are added; a pale to olive-green coloration is developed according to the quantity of bile pigment present. H. W.

Use of Alkalis in Quantitative Analytical Investigations. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1917, **5**, 95—96).—In estimating egg-albumin, asparagine, peptone, and urea by Schloesing's method, the author observed that the results are materially influenced by employing different alkalis. A. J. W.

Rapid Volumetric and Clinical Estimation of Albumin. ED. JUSTIN-MUELLER (*Bull. Sci. Pharmacol.*, 1917, **24**, 29—32; from *Chem. Zentr.*, 1917, i, 977).—The process depends on the union of potassium ferrocyanide with albumin. A mixture of clear, filtered urine (10 c.c.), water (80 c.c.), and acetic acid (5%, 10 c.c.) is titrated with potassium ferrocyanide solution (0·126%). A solution of iron alum (10 grams), acetic acid (10 c.c.), and water (80 c.c.) is used as indicator. If the urine contains 0·5—2 grams of albumin, it is diluted 1 in 10; with higher albumin content, it is diluted 1 in 100. The titration is finished when a drop of the liquid gives an immediate sky-blue coloration with a drop of the indicator. If the urine is insufficiently dilute, the first 3·5 c.c. of the reagent cause a finely divided, voluminous precipitate which obscures the end-point. In this case, either the urine is diluted with ten times its volume of water and the estimation is repeated, or the end-point is determined by means of copper sulphate solution (10%). [Three to four drops of liquid are mixed with one drop of copper sulphate solution. The end-point is indicated by the appearance of a faint reddish-brown coloration.] 0·1 C.c. of the above potassium ferrocyanide solution corresponds, with undiluted urine, with 0·01 gram of albumin per litre. The initial 3·5 c.c. of the reagent are necessary for the saturation of the acidified water, and must therefore be deducted. The urine is free from albumin if the iron-alum reaction occurs immediately after addition of 3·5 c.c. of the reagent. H. W.

Rapid Method for the Estimation of Albumin and Sugar in Urine. EMIL LENK (*Zeitsch. angew. Chem.*, 1917, **30**, ii, 45—48. Compare A., 1916, ii, 163; this vol., ii, 341).—In the estimation of albumin in urine by Esbach's method (precipitation with picric and citric acids), the addition of a very small quantity of finely powdered pumice-stone causes the precipitate to settle completely within ten minutes. When reducing sugars are estimated volumetrically with Fehling's solution, the addition of magnesium sulphate to the copper sulphate solution decreases the time required for the separation of the precipitated cuprous oxide; 10 grams of magnesium sulphate per litre of the copper sulphate solution are sufficient. W. P. S.

A New Process for the Estimation of Reducing Substances in Urine. CHARLES RICHET and HENRY CARDOT (*Compt. rend.*, 1917, **165**, 258—262).—The reagent used is $N/50$-potassium permanganate, made up in $3N/100$-sulphuric acid, and the method is a measure of the reducing substances other than carbamide in the urine. It gives what the authors call the "manganic index" of the urine, that is, the number of litres of the $N/50$-permanganate decolorised in twenty-four hours at the ordinary temperature by the total urine excreted in twenty-four hours. Into each of twelve test-tubes are placed 10 c.c. of the permanganate solution. The urine is diluted to ten times its volume with water, and into the permanganate, in successive tubes, are run 0·5, 0·6, . . . 1·6 c.c. of the diluted urine At the end of twenty-four hours, these tubes are examined for two consecutive tubes, one of which will be decolorised and the other tinged pink. Knowing the amounts of diluted urine run into these tubes, the "manganic index" can be calculated. This will vary in the healthy individual from 50 to 250, but is moderately stable with the same individual on a uniform diet. It bears no relationship to the carbamide excretion or to the total quantity of organic substances other than carbamide present in the urine. W. G.

Culture Media employed in the Bacteriological Examination of Water. IV. Neutral-red Lactose Peptone Media. E. M. CHAMOT and C. M. SHERWOOD (*J. Amer. Chem. Soc.*, 1917, **39**, 1755—1766).—A solution containing 3—4% of peptone, 0·8% of potassium chloride or sulphate, 0·6% of lactose, and 0·008% neutral-red, with an acidity of +1±0·2%, furnishes a sensitive medium for the rapid detection of fæcal pollution by bacteria; the addition of meat-broth increases the sensitiveness, but is not essential. The yellow, fluorescent compound formed by the action of the bacteria is probably dimethyldiaminomethylhydrophenazine, a simple reduction product of neutral-red, into the composition of which ammonia does not enter. The Stokes neutral-red medium is a convenient and trustworthy one for the detection of fæcal contamination in water, and is more sensitive than lactose–bile. T. H. P.

General and Physical Chemistry.

A New Proof of the Existence of Molecules. VI. The Absorption of Light by Molecular and Colloidal Solutions of Sulphur. NILS PIHLBLAD (*Zeitsch. physikal. Chem.*, 1917, **92**, 471—495).—In continuation of previous observations on the absorption of light by colloidal solutions of variable dispersity (compare A., 1913, ii, 2), quantitative measurements have been made of the absorption of ultra-violet light ($\lambda = 250$—$700\ \mu\mu$) by molecular and colloidal solutions of sulphur. The degree of dispersity of the colloidal solutions prepared by different methods varies within wide limits, the most highly disperse solutions being those prepared according to the methods of Wackenroder and Raffo. These solutions were fractionated by Odén's method, and the spectrophotometric observations were thus made on solutions containing particles of approximately the same size.

The results obtained show clearly that the character of the absorption curves changes continuously with decrease in the size of the colloidal particles, and that the absorption of a molecular solution of sulphur in ethyl alcohol corresponds with that of a limiting colloidal solution. The colloidal solutions containing particles for which the average diameter is $550\ \mu\mu$, give a flat absorption curve without any evidence of a maximum. For particles of average diameter $= 160\ \mu\mu$, the absorption is greater, and a maximum is found at $\lambda = 340\ \mu\mu$. In the case of particles of diameter $= 110\ \mu\mu$, the maximum shifts to $\lambda = 280\ \mu\mu$. For more highly dispersive solutions, no maximum was found within the limits of observation, but with diminishing size of the particles the curve of absorption approximates continuously to that of the molecular solution.

Incidentally, it was shown that the absorption of the colloidal solutions is in satisfactory agreement with Beer's law.

H. M. D.

The Light Absorption of an Aqueous Solution of Sodium Sulphate. E. O. HULBERT and J. F. HUTCHINSON (*J. Physical Chem.*, 1917, **21**, 534—535).—Measurements of the absorption of light by a solution of sodium sulphate at temperatures between 20° and 40° show that the absorption undergoes no change at the temperature at which Glauber's salt is transformed into the anhydrous salt.

H. M. D.

Colour and Chemical Constitution. II. Spectra of the Mixed Phthaleins and of the Sulphone-phthaleins. JAMES MOIR (*Roy. Soc. South Africa.* Compare this vol., ii, 349).—Mixed phthaleins containing two different phenol residues, one of which is $C_6H_4{\cdot}OH$, are readily obtained by boiling *p*-hydroxybenzophenone-*o*-carboxylic acid with phenols or amines, whether free or substituted. The spectra of eighteen new phthaleins of this class are described and the relations between them discussed. The spectrum of the mixed phthalein affords a convenient method for the identification of phenols, amines, their ethers, and other derivatives.

The spectra of five sulphone-phthaleins and of six further new derivatives of phenolphthalein have also been examined.

H. M. D.

Absorption Spectra of some Polyhydroxyanthraquinone Dyes in Concentrated Sulphuric Acid Solution and in the State of Vapour. David B. Meek (T., 1917, **111**, 969—988. Compare A., 1916, ii, 364).—The new observations on the absorption of polyhydroxyanthraquinone dyes in the state of vapour and in sulphuric acid solution are compared with the results previously obtained for alcoholic and potassium hydroxide solutions. The nature of the solvent influence is such that the absorption maximum is displaced towards the red end of the spectrum by solution in sulphuric acid and in aqueous potassium hydroxide when comparison is made with alcoholic solutions. Excepting the case of purpurin, the displacement is greater for the potassium hydroxide solutions. The resolution is more pronounced in sulphuric acid solution, and this solvent increases the relative intensity of the absorption towards the violet end of the spectrum.

According to observations on alizarincyanin in various organic solvents, the position of the maximum absorption varies for the most part in agreement with Kundt's rule, but this rule does not apply to acid and basic solvents.

The changes produced by variation in the number and position of the auxochromes show that the approximation of the auxochromes in the benzene nucleus is accompanied by a displacement of the bands towards the red end of the spectrum and by a decrease in the intensity of the bands relative to their breadth. H. M. D.

The Distribution of the Active Deposit of Radium in an Electric Field. S. Ratner (*Phil. Mag.*, 1917, [vi], **34**, 429).—The paper establishes conclusively by a large number of experiments the importance of the electric wind, produced by an electric field in an ionised gas, on the distribution of the active deposit of radium, and has reference especially to the explanation of the origin of the anode activity which is always obtained in greater amount the greater the quantity of emanation employed. When a plate covered with radium-*A* is charged, the electric wind is directed from the active surface and carries away the recoil atoms of radium-*B*. Those atoms that lose their initial charge by recombination with ions may be carried by the wind through long tubes, and even caused to circulate continuously through a system of tubes without showing any tendency to deposit on the walls. In this way, a slow current of discharged recoil-atoms of radium-*B* was caused to circulate through a vessel provided with an insulated electrode, and their distribution in an electric field investigated. Since they are not charged, they should not be affected by an electric field, but it was found they could be collected on a charged plate independently of the sign of the charge. That this is due to the electric wind in the ionised gas, which in this case of uniform ionisation in the gas is partly directed to the plate and partly to the sides of the vessel, was shown by introducing an additional strong source of ionisation into the chamber, so arranged that the electric wind it created was directed towards or away from the charged plate, which in the first case acquired a largely increased activity and in the second acquired practically none. It was shown that the circulation of uncharged radium-*B* recoil-atoms may continue after all the radium-*A* that gave rise to them has disappeared, and charging the electrode for a few minutes after this has occurred causes the plate to become nearly as active as if kept charged throughout the whole period.

Experiments showed that the anode activity obtained when a field is established in a vessel containing radium emanation is due to uncharged particles of the active deposit carried to the anode by the electric wind. If a strong additional source of ionisation was arranged to direct the electric wind from the cathode on the anode, the activity deposited on the anode could be increased to twenty times as great as the cathode activity. In a vessel where large quantities of emanation have been stored, which is therefore coated internally with polonium, the activity collected on the anode is always the same as that collected on the cathode. Using a needle electrode charged to a high potential (15,000 volts), positive or negative, the electric wind from it prevents it receiving any appreciable amount of active deposit. In an uncharged vessel containing emanation, the amount of active deposit on a plate may be largely increased by directing a blast of air against it. The motion of the so-called large radioactive ions in an electric field is to be explained by electric wind effects, not by their carrying a charge. The rate of recombination of radioactive ions is shown to be greater than that of ordinary gaseous ions. F. S.

The Theory of Decay in Radioactive Luminous Compounds. J. W. T. WALSH (*Proc. Roy. Soc.*, 1917, **93** *A*, 550—564).—Rutherford's theory of the destruction of active "centres" in a luminous compound by the passage of the α-ray leads to a simple exponential decay curve, whereas the luminosity of radium luminous compounds decreases exponentially for about 200 days from manufacture, and then the rate of decay decreases, tending to approach a limiting value that is not zero (Paterson, Walsh, and Higgins, *Proc. Phys. Soc.*, 1917, **4**, 215). The theory advanced to explain the discrepancy is that the destroyed active centres recover at a rate proportional to their concentration in the material. This leads to the expression $\log(B_t - m) = Kt$, where B_t is the brightness at time t and m and K are constants, which agrees closely with the observations on eight different samples. For the value of the constants, the full paper must be consulted. In two applications of the theory, (1) the total light emitted by the compound during varying intervals from the time of manufacture, and (2) the variation of the final luminosity of a compound with its content of radium, are calculated. The latter leads to the conclusion that there is no advantage commensurate with cost in using a compound with a greater radium content than 0·2 or at most 0·3 mg. of radium per gram of zinc sulphide. In an appendix, the application to mesothorium compounds is given, and curves are given for the theoretical luminosity against time in years (up to two years) for specimens of mesothorium, respectively, six months, one year, and two years old. F. S.

Radioactivity of Philippine Waters. J. R. Wright and George W. Heise (*J. Physical Chem.*, 1917, **21**, 525—533).—Some ninety different waters, chiefly from springs and flowing wells, have been examined for radioactivity. The waters as a whole show no abnormal features. The highest emanation content met with in a deep-well water was equivalent to 21×10^{-10} grams of radium per litre, and the highest in a spring water to 13×10^{-10} grams. There is no apparent general relation between the chemical quality of a water and its radioactivity.

Tests for the actual radium content of some twenty typical waters showed that the observed radioactivity was due to emanation absorbed from materials with which the ground water had been in contact, and was not due to dissolved radium salts. H. M. D.

Redetermination of the Heat of Vaporisation of Water. J. Howard Mathews (*J. Physical Chem.*, 1917, **21**, 536—569).—The apparatus used is, in principle, the same as that described in a previous paper (Richards and Mathews, A., 1911, ii, 697), but various improvements have been made in detail, including the substitution of a vaporiser made of transparent quartz for the glass vessel previously used, and the employment of a superior type of adiabatic calorimeter.

In preliminary experiments, the possible error due to priming of the water vapour was examined, but it was found that the improved form of apparatus is free from errors arising from this cause. The results obtained in the actual measurements of the heat of vaporisation show clearly the dependence of the values on the rate of condensation, thus confirming the earlier experiments. The relation between the observed heat of vaporisation and the rate of condensation is approximately linear, and by extrapolation the influence of this factor can be eliminated. The value thus obtained for the heat of vaporisation of water at 100° is 539·0 cals. when expressed in terms of the 15° cal. H. M. D.

Heats of Dilution. I. A Calorimeter for Measuring Heats of Dilution. II. The Heat of Dilution of 3*N*-Ethyl Alcohol. D. A. MacInnes and J. M. Braham (*J. Amer. Chem. Soc.*, 1917, **39**, 2110—2126).—The calorimeter described is a modified form of the adiabatic calorimeter devised by Richards (A., 1910, ii, 391, 930), which not only eliminates the heat change due to radiation and conduction, but also the heat effect due to stirring. This result is achieved by making the temperature of the environment slightly lower than that of the calorimeter itself, the difference of temperature required being found by trial. When this temperature difference is correctly adjusted, a thermometer inserted in the calorimeter remains constant for an indefinite length of time.

The calorimeter has been used to measure the heat of dilution of $3N$-ethyl alcohol with varying amounts of water. From the data thus obtained, the authors have calculated the reversible heat of dilution, defined as the heat change which occurs on the addition of 1 mol. of solvent to an infinite quantity of solution. The value of this reversible heat of dilution is 21·80 cal. H. M. D.

Surface Tensions of the Co-existing Layers of Systems of Mutually Soluble Liquids. J. LIVINGSTON R. MORGAN and WARD V. EVANS (*J. Amer. Chem. Soc.*, 1917, **39**, 2151—2171).—The surface tensions of the conjugate solutions formed by water in combination with phenol, amyl alcohol, and triethylamine have been measured at various temperatures by the drop-weight method.

For water and phenol it is found that the curves obtained by plotting the surface tensions of the conjugate solutions against the temperature intersect at 45°, and that the curve for pure phenol passes through the same point. Below 45° the aqueous layer has a lower surface tension than the phenol layer, but at somewhat higher temperatures the order is reversed. The two curves begin to approach each other, however, at some temperature in the neighbourhood of 60°, and become identical at the critical solution temperature, 68·8°.

The surface tension-temperature curves for conjugate solutions of amyl alcohol and water between 0° and 55° diverge with increase in the temperature. The surface tension of both the solutions is much nearer to the value for the alcohol than to that for water.

The curves for triethylamine and water between 25° and 45° point to convergence at about 19°, but accurate measurements could not be made in the neighbourhood of the critical solution temperature by reason of the rapid change in the concentration of the conjugate solutions. It is pointed out as worthy of attention that the aqueous layer increases in surface tension with increase in temperature.

Some observations on the effect produced by the addition of small quantities of water to pure phenol show that this increases the surface tension, the increase attaining a maximum value for a quantity of water which becomes smaller as the temperature falls.

The surface tension of amyl alcohol between 0° and 50° is given by $\gamma = 24{\cdot}450 - 0{\cdot}07308t$, and that of triethylamine between 0° and 40° by $\gamma = 21{\cdot}987 - 0{\cdot}09970t$. H. M. D.

Device for Accelerating Dialysis. H. THOMS (*Ber.*, 1917, **50**, 1235—1240).—The apparatus consists of two chambers (for example, the covers of vacuum desiccators) clamped together with a sheet of parchment between them, and arranged on a framework, so that it can be mechanically rotated about the plane of the membrane. One chamber contains water and the other the liquid to be dialysed, both being only half full. As the apparatus revolves, the liquids glide over the membrane and the separation of the crystalloid is two or three times as efficient as in stationary dialysers, especially in the case of dilute solutions.

The process is termed "gliding dialysis," and is specially designed for the preparation of stable fruit syrups which contain the fragrant constituents and enzymes of the fruit juice in the undecomposed state. J. C. W.

Diffusion and Osmosis under the Influence of Electrocapillary Forces. TONI HAMBURGER (*Zeitsch. physikal. Chem.*, 1917, **92**, 385—420).—According to Girard (compare A., 1914, ii, 718), the phenomena of diffusion and osmosis are largely influenced by the electrical charge of the membrane concerned. The experiments described consist for the most part of observations similar to those previously made by Girard, but the results obtained differ appreciably in some respects and lead to the conclusion that electrocapillary forces do not play any essential part in connexion with the phenomena of diffusion, although the osmosis is influenced by the electrical charge of the membrane. The variation in the magnitude and sign of the charge is probably to be explained in terms of adsorption and hydration of the ions. H. M. D.

Dissociation of Complex Double Salts in Aqueous Solutions. HAROLD L. MAXWELL (*Chem. News*, 1917, **116**, 247—250).—The changes which occur when solutions of double salts are allowed to diffuse into water have been examined in a series of experiments with sodium cadmium bromide, ammonium zinc bromide, ammonium copper chloride, and ferrous ammonium sulphate. The results show that diffusion leads to a partial separation of the component simple salts. H. M. D.

Vapour-pressure Isotherms of Substances with Gel Structure. WILHELM BACHMANN (*Zeitsch. anorg. Chem.*, 1917, **100**, 1—76).—The ultra-microscopic structure of gelatin and silica gels has been demonstrated (A., 1912, ii, 145), but concentrated gels are found to be amicroscopic, and other methods must be used to determine their structure. Zsigmondy has shown (A., 1911, ii, 880) that the dimensions of the structure may be calculated from the vapour pressure isotherms, the vapour pressure of liquid enclosed in very fine canals being lower than that of the same liquid with a free surface. The theory is only applicable to gels in which the liquid is chemically indifferent towards the enclosing substance. In addition to gelatin, a natural silica gel (hydrophane from Hubertusburg), permutite, and coconut charcoal have now been investigated by this method. A vacuum apparatus is used (A., 1912, ii, 641), and the vapour pressure is regulated by using mixtures of alcohol and glycerol, benzene and paraffin, or sulphuric acid. In all cases the ascending and descending vapour pressure isotherms form a characteristic hysteresis diagram, similar to those obtained by van Bemmelen for colloidal hydroxides. The type is independent of the nature of the enclosed liquid and of the gel skeleton. The relative contraction which occurs when the liquid is completely removed from the pores of a gel has been determined in several cases. Experiments with hardened gelatin gels indicate that the canals are from 30 to 100 times smaller than was supposed by Bütschli in his honeycomb theory of gels. Canals of 700—800 $\mu\mu$ diameter would have no appreciable effect on the vapour pressure, and the discontinuities observed microscopically must be regarded as subsidiary to the main structure of the gel. The dehydration and hydration curves of coconut charcoal exhibit two hysteresis areas, indicating systems of pores of different dimensions.

Permutite, according to its behaviour with benzene, has a structure comparable with that of old solid silica gels, and its largest pores are relatively coarse (20 $\mu\mu$ and more in diameter). Hydrophane behaves as a very old silica gel, artificial gels of increasing age giving curves which tend to approach those of hydrophane as a limiting conditon.
C. H. D.

A New Method of Preparing Colloids. Jnanendra Chandra Ghosh (*Rep. Indian Assoc. Sci.*, 1915, 87—89).—If a dilute solution of a salt of a heavy metal is electrolysed with a large platinum anode and a platinum point cathode, and electric oscillations are impressed on the circuit, the metal is not deposited on the cathode, but remains suspended in the form of a colloidal solution. Silver and mercury sols have been obtained in this way, and in the case of silver it has been found that the quantity of the sol is proportional to the total quantity of electricity furnished by the source of the direct current.
H. M. D.

Mechanism of the Precipitation Process. H. R. Kruyt and Jac. van der Spek (*Chem. Weekblad*, 1917, **14**, 950—953).—A theoretical paper, discussing the influence of the nature of the ions and the concentration on the precipitation of colloidal solutions.
A. J. W.

Physico-chemical Analysis of Colloidal Ferric Hydroxide. Wolfgang Pauli and Johann Matula (*Kolloid Zeitsch.*, 1917, **21**, 49—63).—An attempt has been made to ascertain the constitution of hydrosols and in particular to trace the origin of the electrical charge of the colloidal particles of ferric hydroxide by potential difference and conductivity measurements and observations on the coagulation produced by the addition of electrolytes.

The data suggest that ferric hydroxide sol is to be regarded as a complex salt, the anion of which is identical with that in the ferric salt used in the preparation of the sol. From the electrometric data and chlorine estimations for a sol prepared from ferric chloride, it would seem that the ionisation of the complex chloride corresponds with that of a moderately strong electrolyte. By the addition of other electrolytes having an ion in common, changes are brought about which can be readily interpreted as mass action effects. The coagulating power of added electrolytes appears also to be determined by the solubility product for the combination of the colloid ion and the anion of the coagulant. According to this view, inorganic colloids show a close resemblance in their behaviour to that of typical electrolytes.

The question of the structure of the complex colloid ion is not nearly so clearly indicated by the experiments described, but the facts suggest that the sol may be represented by the formula $x\mathrm{Fe(OH)_3} \cdot y\mathrm{Fe}^{\cdots}3y\mathrm{Cl}'$. This formula accords with the fact that chlorine ions only are removable by dialysis. The cations accompanying the chlorine ions are hydrogen ions, and since the electrometric measurements indicate that such sols are neutral, it would seem that the corresponding hydroxyl ions react with the ferric ions to produce ferric hydroxide, thereby leading to an increase in the value of x. The sol particles thus increase in size and become more susceptible to the action of coagulants. Changes in viscosity which accompany the ageing of colloids may possibly be explained in a similar manner.

The theory put forward is discussed in relation to other hypotheses which have been advanced to account for the characteristic properties of colloids and also to the micellary theory of colloid structures. H. M. D.

The Molecular Condition of Acetic Acid in Boiling Benzene and in the Saturated Vapour from the Solution.

Ernst Beckmann, Otto Liesche, and Werner Gabel (*Zeitsch. physikal. Chem.*, 1917, **92**, 421—432).—When an associating volatile substance like acetic acid is dissolved in a non-associating solvent like benzene, the complete statement of the equilibrium conditions at the boiling point of the solution involves a knowledge of the dissociation equilibrium in the vapour and liquid phases and of the distribution of the two kinds of molecules between the vapour and liquid phases.

Measurements have been made of the change produced in the boiling point of benzene by the addition of varying quantities of acetic acid and of the composition of the co-existing liquid and vapour phases.

Denoting by p_1 and p_2 the partial pressures of the single and double molecules of acetic acid in the vapour, and by P_1 and P_2 the osmotic pressures in the liquid solution, then the equilibrium relations may be expressed by $p_2/p_1^2=\chi$, $P_2/P_1^2=k$, $P_1/p_1=l_1$, and $P_2/p_2=l_2$, from which $\chi l_2/kl_1^2=1$.

As the concentration of acetic acid increases, the difference, Δ, between the boiling point of the solution and that of the solvent, which is at first negative, increases to a maximum, then decreases, and finally becomes positive. For the solution for which $\Delta=0$, the value of g (acetic acid per 100 grams of liquid benzene) is 6·275 and the value of γ (acetic acid per 100 grams of benzene vapour) is 4·796. From these data and $\chi=20·69$, the following values of the equilibrium coefficients are derived: $k=1·350$, $l_1=98·64$, and $l_2=634·9$.

If n is the number of molecules of acetic acid in the liquid and ν the corresponding number for the vapour, then the change in the boiling point is given by $\Delta=K(n-\nu)$, in which K is the normal molecular elevation of the boiling point. The values of Δ, calculated from this equation by the aid of the above equilibrium constants, are found to be in satisfactory agreement with the observed values. H. M. D.

Systems of many Components. W. Eitel (*Zeitsch. anorg. Chem.*, 1917, **100**, 95—142).—When the number of components in a system is greater than four, the ordinary geometrical representation of the phase relationships is impossible. Such systems may be represented by an application of polydimensional geometry (compare Boeke, this vol., ii, 178). An N-component system is represented by a 'polytope,' T_N, of $N-1$ dimensions, and the number of binary, ternary, and higher systems may be calculated in each case. Thus a 5-component system includes 10 binary, 10 ternary, and 5 quaternary systems. Such polytopes may be projected on to a plane, and the polygons thus obtained have $N-1$ sides, the remaining point being placed at the centre. Details of the geometrical construction are given, and the methods of projection are described, being worked out in detail for the case of a 5-component system, in which all the components separate as pure solid phases. A few special cases of solid solution are also examined. C. H. D.

The System Aniline-Hexane. Donald B. Keyes and Joel H. Hildebrand (*J. Amer. Chem. Soc.*, 1917, **39**, 2126—2137).—Normal liquids are with few exceptions miscible in all proportions, and as a result of the examination of 500 pairs, the only liquids of this type found to give two liquid systems were aniline and pentane or hexane, and also naphthylamine and pentane or hexane.

With the view of finding an explanation for the deviations from Raoult's law, the physical properties of mixtures of aniline and hexane have been examined. These properties include the vapour pressure, heat of mixing, surface tension, change of volume on mixing, compressibility, and the mutual solubility in its dependence on the temperature.

The vapour pressures show a strong positive deviation from the requirements of Raoult's law, the deviations being much greater than those which follow from the assumption that the aniline is associated to form double molecules or molecules of still greater complexity. The formation of mixtures is accompanied by heat absorption, by expansion for mixtures rich in hexane, and by contraction for mixtures rich in aniline. The surface tension of the mixtures is less than that given by the mixture rule, whilst the compressibility for mixtures rich in hexane is greater, and for mixtures rich in aniline less than that calculated by the mixture rule. The theoretical significance of the observations is discussed briefly.

H. M. D.

Piezo-chemical Studies. XIV. Influence of Pressure on the Velocity of Reaction in Condensed Systems. III. ERNST COHEN and A. M. VALETON (*Zeitsch. physikal. Chem.*, 1917, **92**, 433—470. Compare A., 1915, ii, 246).—The apparatus employed by Cohen and de Boer in the investigation of the influence of pressure on the rate of inversion of sucrose in presence of hydrochloric acid (A., 1913, ii, 687) has been improved in detail and used in further experiments in which acetic acid was used as catalyst at 25°, 35°, and 45° under pressures reaching up to 1500 atmospheres.

The results obtained show that the velocity-coefficient increases as the applied pressure increases, but that the rate of increase is much smaller at pressures above about 1000 atmospheres. When the numbers are corrected for the change in concentration due to the compressibility of the solutions, it is found that the velocity-coefficient is independent of the pressure at pressures above 1000 atmospheres.

On comparing the results with those obtained previously by Stern, considerable discrepancies are found. H. M. D.

Contact Catalysis. I. WILDER D. BANCROFT (*J. Physical Chem.*, 1917, **21**, 573—602).—The phenomena of contact catalysis are discussed, with particular reference to the theories which have been advanced in explanation of these effects. The author arrives at the conclusion that contact catalysis depends on adsorption and that the catalytic effect may in some cases be explained entirely on the basis of the increased surface concentration. Solids which act as catalysts may be considered as equivalent to a solvent, and hence may cause a displacement of the equilibrium. The displacement is favourable to the system which is more strongly adsorbed.

As a consequence of selective adsorption, the products obtained may vary with the nature of the solid catalyst. H. M. D.

The Conception of the Chemical Element. K. FAJANS (*Jahrb. Radioaktiv. Elektronik*, 1917, **14**, 314—352).—A long discussion of how the accepted facts in regard to isotopic elements may be reconciled with the current conception of the chemical element originating with Boyle is summarised as follows. It is not justifiable to consider iostopic elements as the same element and isotopes as different kinds of the same element. The common methods of chemical analysis only fail to distinguish between isotopes if they are qualitative. The difference in equivalent shows that isotopes cannot be considered as the same element. It is more convenient to regard isotopes as different elements and to create a new conception "elementary type" to include them. Although the accepted elements may themselves be mixtures of isotopes, until this is demonstrated they should be called elements—an element being considered a substance not yet, rather than one that cannot be, separated. Those, not yet separated into their constituents, but which we can with certainty conclude are mixtures, are not to be considered elements. The definition of an element proposed is "a substance that has not been separated into simpler constituents and is not known to be a mixture of other substances." According to this definition, there are 92 elementary types or pleiads. Of 77 types only one element, of 6 types no element, and of the remaining 9 types several (two to seven) elements are known, making the total number of elements, or kinds of atoms, known to-day as 117.

F. S.

Distilling Head. Orlo Stearns (*J. Ind. Eng. Chem.*, 1917, **9**, 972—973).—The bulb forming the essential part of the apparatus is "heart-shaped" in section; the tube leading to the condenser leaves the depression at the top of the bulb, and is inclined upwards at an angle of 110° from the vertical before it is bent downwards to join the top of the condenser. This tube diminishes in diameter from 15 mm., where it leaves the bulb, to 7 mm. at a distance of 4 cm. above the bulb. The tube leading from the distillation flask enters the lower part of the bulb and extends into the latter, this part of the tube being bent over so that the end points downwards inside the bulb. A small hole is provided at the bottom of the portion of the tube which is inside the bulb so that liquid may return to the flask. W. P. S.

Mercury Vapour Pumps for Operating against High Pressures. Charles A. Kraus (*J. Amer. Chem. Soc.*, 1917, **39**, 2183—2186).—The pump described has been designed with the object of avoiding the necessity for the use of an auxiliary pump giving a relatively high vacuum.

It consists of two mercury pumps operating in series, the initial reduction in pressure being attained by the use of an ordinary water-jet pump. The evacuation is effected by a rapid stream of mercury vapour which passes through a suitable nozzle, each pump being provided with a boiling tube and water-cooled condenser. The first of the two mercury pumps operates against a back pressure as high as 40 mm. and gives a vacuum of less than 1 mm. The second operates against back pressures up to 7 or 8 mm. and gives a vacuum as good as that which is attainable by other pumps of this type. H. M. D.

New Shaking Apparatus and their Application. H. Thoms (*Ber.*, 1917, **50**, 1242—1244).—A cage for a bottle, or a plate to which tubes can be clamped, is fitted into a framework so that it can be rotated about its axis (compare this vol., ii, 561).

J. C. W.

The Nomon—A Calculating Device for Chemists. Horace G. Deming (*J. Amer. Chem. Soc.*, 1917, **39**, 2137—2144).—The nomon, or nomographic reckoner, is a calculating chart with a degree of precision from five to ten times that of an ordinary 10-in. slide rule, by means of which it is possible to multiply, divide, square, cube, and to extract square and cube roots with an average error of about one unit in the fourth place. Its employment in chemical practice is illustrated by examples. H. M. D.

Lecture Experiment :—Preparation of Sodium. SIEGFRIED WIECHOWSKI (*Chem. Zeit.*, 1917, **41**, 739).—A stick of sodium hydroxide is grooved in the direction of its length and placed in a shallow glass dish. A knitting-needle is brought into contact with the sodium hydroxide at each end of the narrow trough, pressure being applied so as to make the contact as intimate as possible. After ten to fifteen minutes, the sodium hydroxide has absorbed sufficient moisture to make the system a conductor, and if the needles are connected through a suitable resistance with a 110 or 220 volt circuit, the current passes and metallic sodium is deposited at the cathode. To prevent oxidation, the rod of sodium hydroxide may be covered with a layer of liquid paraffin. H. M. D.

Inorganic Chemistry.

An Improved Hydrogen Chloride Generator. O. R. SWEENEY (*J. Amer. Chem. Soc.*, 1917, **39**, 2186—2188).—The generator consists of a separating funnel which is half filled with strong sulphuric acid. This is fitted with a two-holed rubber stopper. Through one hole is passed a piece of capillary tubing about 40 cm. in length, the upper end of which is sealed on to a dropping funnel containing hydrochloric acid (D 1·18). When the hydrochloric acid is allowed to flow into the sulphuric acid, hydrogen chloride is given off in a steady stream, the rate of generation of the gas being controlled by the tap on the dropping funnel. The spent sulphuric acid, which is readily discharged, contains very little hydrogen chloride, and may be used for many laboratory operations. H. M. D.

Recovery of Perchlorate Residues obtained in Potassium Estimations. A. VÜRTHEIM (*Chem. Weekblad*, 1917, **14**, 986—988).—The perchlorate residues are converted into potassium perchlorate, from which the perchloric acid is liberated by distillation under reduced pressure with sulphuric acid. The acid evolved is absorbed by means of water. A. J. W.

Reduction of Selenic Acid. E. B. BENGER (*J. Amer. Chem. Soc.*, 1917, **39**, 2171—2179).—Contrary to Mitscherlich's statement, selenic acid is reduced by hydrogen sulphide. The rate of reaction increases with the temperature and with the concentration of the acid. The complete reaction may be represented by the equation $3H_2S + H_2SeO_4 = Se + 3S + 4H_2O$, but the mechanism is more complicated than this equation suggests.

Selenic acid is also reduced by sulphur dioxide, the reaction taking place in two stages represented by the equations $H_2SeO_4 + SO_2 = H_2SO_4 + SeO_2$, $SeO_2 + 2H_2O + 2SO_2 = 2H_2SO_4 + Se$.

The reducing action of sulphur and selenium has also been examined. In the anhydrous condition, selenic acid is reduced by sulphur at about 60°; in aqueous solution, the reaction requires a higher temperature. Selenium reduces the acid in aqueous solution at the ordinary temperature. H. M. D.

Reduction of Telluric Acid. E. B. Benger (*J. Amer. Chem. Soc.*, 1917, **39**, 2179—2183).—Aqueous solutions of telluric acid of all concentrations are slowly reduced by hydrogen sulphide and by sulphur dioxide. In 30% solution, the acid is reduced by sulphur, selenium, and tellurium when heated in a sealed tube at 110°.

By comparison with selenic acid, telluric acid is not so easily reduced. Although this is not in accordance with the behaviour expected according to the periodic grouping of the elements of the sulphur group, it is in harmony with the thermochemical data.
H. M. D.

The Distillation of Mixtures of Nitric and Sulphuric Acids. Paul Pascal (*Compt. rend.*, 1917, **165**, 589—591).—A study of the ternary mixture water–sulphuric acid–nitric acid. Two diagrams are given, one showing the surface of the boiling points under normal pressure, the second showing the variations in the concentrations of nitric acid in the vapours emitted on distillation.
W. G.

The Effect of the Partial Pressure of Oxygen on Combustion. H. C. Dollwig, A. C. Kolls, and A. S. Loevenhart (*J. Amer. Chem. Soc.*, 1917, **39**, 2224—2231).—In mixtures of oxygen and nitrogen at atmospheric pressure the flame of a paraffin or a tallow candle, and of an ethyl alcohol (99·8%) lamp, with an asbestos wick are extinguished at the following partial pressures of oxygen: 116 mm. of mercury for the candle and 112·7 mm. for the alcohol. On rapidly evacuating a chamber filled with air, the flames of the candle and the lamp are extinguished at the following partial pressures of oxygen: 19 mm. of mercury for the candle and 27 mm. for the alcohol. W. G.

The Bunsen Flame under Diminished Pressure. L. Ubbelohde and R. Anwandter (*J. Gasbeleucht.*, 1917, **60**, 225—232, 242—246, 268—273; from *Chem. Zentr.*, 1917, ii, 271—272).—The chemical actions which usually occur in the gas flame may be represented by the equations: (1) $CO + H_2O \rightleftharpoons CO_2 + H_2$; (2) $2CO + O_2 \rightleftharpoons 2CO_2$; (3) $2H_2O + O_2 \rightleftharpoons 2H_2O$. Diminution of pressure disturbs the equilibria in (2) and (3) in such a manner that the dissociation of carbon dioxide and water vapour is increased.

It might therefore be expected that the rate of reaction would be so diminished by decreasing the pressure (in consequence of the slow combustion and the increased dissociation and resulting depression of temperature) that a closer study of the chemical processes would be rendered possible. For details of apparatus, the original paper must be consulted.

The authors are led to the following conclusions. The maximum velocity of inflammation of theoretical mixtures of carbon monoxide and air increases from 42 cm. per second at 760 mm. to 60 cm. per second at about 300 mm.; at lower pressures the maximum sinks, and has the value 47 cm. per second at 173 mm. With decreasing pressure, equilibrium becomes less completely established at 1 mm. above the inner cone; at 760 mm. the theoretical mixture of carbon monoxide and air is so far burnt as to contain 26% CO_2, whilst at 162 mm. only about 5% CO_2 is present. Consequently, the calorimetric temperature of the flame is 2020° at 760 mm. and 730° at 162 mm. The probable temperature is about 300° below the calorimetric at 760 mm.; with decreasing pressure the difference probably becomes less pronounced until, at about 140 mm., the temperatures are identical. Below 140 mm., combustion is so incomplete that a flame can no longer be obtained with the ordinary Bunsen burner. With increasing previous heating of the gases, combustion becomes more difficult, and consequently also the attainment of equilibrium. Delayed combustion above the inner cone becomes more pronounced with decreasing pressure. At low pressures, the greater portion of the gases undergoes combustion above the visible portion of the inner cone (above the luminous zone). The maximum temperature in flames burning under low pressure lies about 5—7 mm. above the top of the inner cone. At a pressure of 400 mm. the luminous zone begins to show measurable thickness (at 400 mm., 0·3 mm.; at 200 mm., about 1·6 mm.; at 145 mm., about 2·7 mm.). It has not been experimentally proved whether this phenomenon is caused by an actual thickening of the zone or by oscillation of an extremely narrow zone. Under ordinary conditions, the theoretical mixture of carbon monoxide and air is only burnt to about 26% CO_2 in the inner cone. H. W.

Recovery of Potassium and Aluminium Salts from Mineral Silicates. J. C. W. Frazer, W. W. Holland, and E. Miller (*J. Ind. Eng. Chem.*, 1917, **9**, 935—936).—Finely ground felspar is mixed with four-fifths of its weight of potassium hydroxide or an equivalent quantity of sodium hydroxide, and a small quantity of water, the mixture is dried, and heated for one hour at 300°. The mixture is then treated with water and the insoluble portion is separated by filtration. This insoluble portion has the composition $KAlSi_2O_6$; the alkali used passes into the filtrate and may be recovered. The insoluble compound is then treated with a quantity of hydrochloric acid equivalent to the potassium content; potassium chloride is formed, whilst the aluminium silicate remains insoluble. The latter is readily decomposed by sulphuric acid, yielding aluminium sulphate. W. P. S.

Pure Sodium Chloride. VERNON C. SHIPPER (*Chem. News*, 1917, **116**, 213—214).—Estimations have been made of the quantity of potassium chloride in various samples of sodium chloride purified by fourfold recrystallisation from water. The results indicate that the potassium chloride can be eliminated by recrystallising the sodium chloride a sufficient number of times.

H. M. D.

Studies of the Carbonates. III. Lithium, Calcium, and Magnesium Carbonates. CLARENCE ARTHUR SEYLER and PERCY VIVIAN LLOYD (T., 1917, **111**, 994—1001. Compare this vol., ii, 196).—In continuation of the investigation of the constitution of solutions of the alkali metal carbonates, experiments have been made with lithium, calcium, and magnesium carbonates.

The solubility of lithium carbonate in carbonic acid solutions of varying concentration indicates that ionisation takes place in two stages, the degree of ionisation being the same as for sodium carbonate.

The ionic solubility product of calcium is $[Ca^{\cdot\cdot}]\cdot[CO_3'']=71\cdot9\times10^{-10}$, which is lower than the values previously recorded. This gives $[Ca^{\cdot\cdot}]=14\cdot6\times10^{-5}$ for a saturated solution of calcium carbonate in pure water at 25°. In this solution, the carbonate is hydrolysed to the extent of 66%.

Crystalline magnesium carbonate ($MgCO_3,3H_2O$) is decomposed by water, and equilibrium conditions have not been obtained. The reaction approximates to

$$5MgCO_3+2H_2O=3MgCO_3,Mg(OH)_2+Mg(HCO_3)_2.$$

In presence of sufficient carbonic acid, the carbonate is stable, and from Engel's data at 12·5°, the ionic solubility product

$$[Mg^{\cdot\cdot}]\cdot[CO_3'']=141\times10^{-6}.$$

H. M. D.

Silver Electro-colloids. G. REBIÈRE (*Bull. Sci. Pharmacol.*, 1917, **24**, 193—204; from *Chem. Zentr.*, 1917, ii, 276—277).—Electro-hydrosols of silver are obtained by passing a suitable current through silver electrodes immersed in water contained in a hard glass beaker cooled in ice-water. The electrodes are placed 1 cm. below the surface; 110—120 volts and 5—10 amperes should be used. When the current is passed, a smoky arc soon appears between the electrodes, which must be maintained by suitable regulation. The separation of colloidal silver is accompanied by a reverse current. In general, the method is similar to that used by Svedberg in the preparation of solutions of metallic colloids in organic media, except that water is here employed. The silver hydrosols appear cloudy by reflected, clear by transmitted light, and are variously coloured (grey, yellow, violet, green, and red), depending on the size of the particles and the nature of the intercorpuscular liquid. The concentration of the metal is of secondary importance.

For the determination of the chemical composition of the electro-hydrosols, a separation of the corpuscles and intercorpuscular liquid is essential, which may be effected by several methods (coagulation by electrolytes, ultra-filtration, centrifuging, coagulation, dissociation, etc.). Quantitative results can only be obtained by precipitation with very dilute electrolytes and subsequent centrifuging. Barium nitrate is added to the hydrosol in such quantity that the concentration of the salt is approximately $1/5000N$; after a few minutes, the mixture is centrifuged at a rate of at least 9000 revolutions per minute. In this manner, the components are obtained in the same ratio as that in which they exist in equilibrium in the electro-hydrosol. Silver is estimated by the cyanide method. The silver hydrosols appear deeper brown by transmitted light in proportions as they contain less silver; with increasing silver content, the colour becomes more markedly green. The electrical conductivity increases with increasing silver content. The purity is expressed by the formula $100(Ag\delta/Agt)$. The colloidal silver precipitated from the hydrosols is a dull, anhydrous, black powder which sometimes has a yellow lustre and shines when rubbed. It absorbs carbon dioxide from the air, dissolves readily in nitric acid with evolution of nitrous fumes, yields metallic silver and chlorine with hydrochloric acid, and is decomposed at a bright red heat into silver and oxygen. It therefore appears to be a lower oxide of silver containing Ag 96·4—97·98%. The conductivity of the intercorpuscular liquid obtained by ultrafiltration is higher than that of the water used; it is therefore a solution of silver oxide. H. W.

The Oxy-salts of the Alkaline Earth Metal Haloids. Equilibria in Ternary Systems. II. J. Milikan (*Zeitsch. physikal. Chem.*, 1917, **92**, 496—510. Compare this vol., ii, 257).—The equilibrium conditions in the ternary systems formed by the alkaline earth chlorides, hydrogen chloride, and water have been examined at 25°.

In the system $CaCl_2$–HCl–H_2O, the solution containing 44·50% $CaCl_2$ and 3·3% HCl is in equilibrium with the solid phases $CaCl_2,6H_2O$ and $CaCl_2,4H_2O$, and the solution containing 28·48% $CaCl_2$ and 21·40% HCl with the solid phases $CaCl_2,4H_2O$ and $CaCl_2,2H_2O$.

In the system $SrCl_2$–HCl–H_2O, the solid phases occurring at 25° are $SrCl_2,6H_2O$ and $SrCl_2,2H_2O$, and these co-exist in equilibrium with a solution containing 2·11% $SrCl_2$ and 27·14% HCl.

For the system $BaCl_2$–HCl–H_2O, the equilibrium data at 30° have been previously published by Schreinemakers (A., 1912, ii, 760). By combining the data for the system salt–acid–water with the data for the system salt–base–water (previous paper, *loc. cit.*), a survey of the equilibrium relations in both alkaline and acid solutions is obtained. H. M. D.

Formation of Tricalcium Aluminate. Edward D. Campbell (*J. Ind. Eng. Chem.*, 1917, **9**, 943—946. Compare A., 1914, ii, 772).—Tricalcium aluminate seems to be best formed when the compound $5CaO,3Al_2O_3$ is kept for a long time in contact with lime at a temperature just above the melting point of the eutectic solution of lime (1395°), but below the melting point of the pure compound, $5CaO,3Al_2O_3$ (1455°). The binary system of lime and alumina, containing more than 47·8% CaO, should be regarded as a solution of lime in the compound $5CaO,3Al_2O_3$. Tricalcium aluminate may be considered to be a metastable saturated solid solution of lime in $5CaO,3Al_2O_3$, or as $5CaO,3Al_2O_3$ with 4 mols. of CaO of crystallisation, rather than as a stable phase in the strict sense of the word. W. P. S.

The Refractory Properties of Magnesia. H. Le Chatelier and B. Bogitch (*Compt. rend.*, 1917, **165**, 488—491).—A comparison of some six types of magnesia bricks for furnaces with reference to their resistance to crushing with rise in temperature. The best type, as regards high magnesium oxide content, showed a sudden fall in resistance at between 1500° and 1600°, less pure types showing a similar fall at between 1300° and 1400°. A ferrochrome brick similarly compared showed a rapid loss of solidity at 1100°. W. G.

Theory of the Electrolytic Formation of Lead Tetrachloride. Robert Kremann and Hermann Breymesser (*Monatsh.*, 1917, **38**, 113—120).—The authors have investigated the mechanism of the formation of lead tetrachloride by the electrolytic oxidation of a solution of hydrochloric acid (D 1·18) saturated with lead chloride (Elbs and Nübling, A., 1903, ii, 727). There are two possibilities: (1) the tetrachloride is directly formed on the anode and acts as a depolariser on the carbon electrode, or (2) lead chloride is formed on the anode and this then reacts in the solution with chloride liberated from the carbon electrode. To decide between the two possibilities the authors have determined the decomposition voltage at 0° and 21° of solutions of hydrochloric acid (D 1·18) and of similar solutions saturated with lead chloride. It is found that two breaks occur in each of the current-voltage curves. The first break occurs at 0·83 volt at 0° and 0·87 volt at 21°, and is the same for both solutions. The second occurs for hydrochloric acid alone at 0·99 volt at 0° and 0·95 volt at 21°, whilst for hydrochloric acid saturated with lead chloride the values are 1·04 volts at 0° and 1·00 volt at 21°. From these results it is shown that the formation of lead tetrachloride is a secondary process between the lead chloride and chlorine formed respectively on the lead and carbon anodes, and differs in no way from the chemical method of formation of this substance as described by Friedrich (A., 1893, ii, 415). J. F. S.

The Heterogeneity of Steels. G. Charpy and S. Bonnerot (*Compt. rend.*, 1917, **165**, 536—540).—The authors find that the cupric reagent of Le Chatelier and Lemoine gives much clearer results than the other reagents commonly used for the attack of steels prior to microscopic examination. They consider that the study of the heterogeneity of steels should be directed to two points, namely, (1) the distribution and relative dimension of the juxtaposed elements, and (2) the difference of quality between these elements. W. G.

Electrolytic Deposition of Alloys and their Metallographic Examination. VII. Experiments on the Cathodic Preparation of Pyrophoric Deposits from Glycerol-Water Solutions of Iron Salts with additions of other Salts, particularly Cerous Chloride. ROBERT KREMANN, RUDOLF SCHADINGER, and RICHARD KROPSCH (*Monatsh.*, 1917, **38**, 91—111. Compare A., 1914, ii, 96, 422, 615, 616).—In a previous paper experiments are described whereby pyrophoric alloys were prepared from solutions of iron salts in the presence of glycerol and magnesium salts. The present paper describes similar experiments in which cerous chloride is substituted for magnesium chloride. The experiments were carried out at various current densities and potential differences. The solutions contained quantities of glycerol amounting to 75% and 50% of the whole solution. The hardness and pyrophoric character of the various deposits were determined in every case. It is shown that the substitution of cerous chloride for magnesium chloride does not increase the pyrophoric character of the deposit. In some cases a comparatively large amount of cerium is deposited along with the iron, but in no case is the amount so large as that contained in the technical pyrophoric cerium alloys. The presence of large amounts of cerium in certain cases is regarded as being due to secondary causes, and not to direct electrolytic deposition. A series of microphotographs of the various cathode deposits described is appended to the paper. J. F. S.

Ferric Oxide and Alumina. FRANCIS H. SCHEETZ (*J. Physical Chem.*, 1917, **21**, 570—572).—The yellow colour in bricks has been shown previously to be due to a yellow modification of anhydrous ferric oxide, which is rendered stable by alumina. In reference to this effect, some experiments have been made, in which solutions containing ferric and aluminium sulphates were precipitated with sodium carbonate, sodium hydroxide, and lime, the washed precipitates being dried and then heated gradually up to 1000°. The precipitates obtained with lime water gave a buff-coloured product provided that the oxide mixture contains less than 8% of ferric oxide. The buff colour is not obtained when sodium carbonate or hydroxide is the precipitant. H. M. D.

The Arrangement of the Atoms in Tungsten. P. DEBYE (*Physikal. Zeitsch.*, 1917, **18**, 483—488).—The *X*-ray method for the investigation of crystal structure, described previously (compare this vol., ii, 437), has been applied in the investigation of samples of powdered tungsten. In spite of the fact that *X*-rays are very strongly absorbed by the metal, it has been found possible to obtain interference figures, from which it is clear that tungsten crystallises in cubic forms, and that the elementary space lattice is a cube with a centrally situated point, the length of the edge of the cube being $3{\cdot}18 \times 10^{-8}$ cm. H. M. D.

The Search for Two Unknown Metals (Neomolybdenum and Neotungsten). M. Gerber (*Mon. Sci.*, 1917, [v], **7**, 73—83, 121—127, 169—177, 219—226).—The author claims to have discovered that neither molybdenum nor tungsten is a simple substance, each of these metals being accompanied by closely related, hitherto unrecognised elements, to which the names *neomolybdenum* and *neotungsten* have been given. It is suggested that the two new elements will fill the two unoccupied positions in the periodic table in group VII below manganese, their atomic weights being estimated approximately as: neomolybdenum = 99·9, neotungsten = 188. Chemically, each of the new elements is very closely related to the element with which it is found associated, and spectroscopically is quite indistinguishable therefrom. On this account it is suggested that each new element is a metallic isotope of the element with which it is associated, by analogy with the two forms of lead, which appear to be chemically and spectroscopically identical.

Neomolybdenum was separated from molybdenum by fractional crystallisation of a specimen of ammonium molybdate prepared from molybdenite from Glen Innis, New South Wales. The most soluble fraction, when analysed, gave for the metal an atomic weight = 100 (Mo = 96), and, moreover, the acidic oxide obtained by heating this ammonium salt was far more volatile than ordinary molybdic acid. The properties of neomolybdenum do not agree with those of the nipponium of Ogawa (A., 1908, ii, 952) supposed to be ekamanganese.

From soluble metatungstic acid the author has prepared the ammonium *iso*tungstate described by Laurent, the existence of which has been since denied or overlooked. In the *iso*tungstic acid prepared from this, the metal had an atomic weight = 186·5 to 187 (W = 184). This *iso*tungstic acid, it is supposed, contains neotungsten. A long historical account of the tungstates is given. E. H. R.

Mineralogical Chemistry.

Minasragrite, a Hydrous Sulphate of Vanadium. Waldemar T. Schaller (*J. Washington Acad. Sci.*, 1917, **7**, 501—503).—This mineral occurs abundantly at Minasragra, Peru, as a blue efflorescence on patronite, of which it is an alteration product. It is also being formed at the present time on museum specimens of patronite. On the specimen examined are the primary minerals patronite, quisqueite, and bravoite, and the secondary minerals minasragrite, melanterite, morenosite, and gypsum. The mineral is probably monoclinic or triclinic, and has refractive indices $\alpha=1\cdot515$, $\beta=1\cdot525$, $\gamma=1\cdot545$. It is readily soluble in cold water; analysis of impure material gave:

V_2O_4.	FeO.	NiO.	CaO.	SO_3.	Insol. in water.	H_2O (diff.).
5·29	0·97	1·92	0·46	10·92	66·16	[14·28]

Deducting iron, nickel, and calcium as melanterite, morenosite, and gypsum respectively, the figures for the vanadium sulphate become: V_2O_4, 24·64; SO_3, 33·17; H_2O, 42·19%, corresponding with the formula $V_2O_4,3SO_3,16H_2O$, which is interpreted as a hydrated acid vanadyl sulphate, $(V_2O_2)H_2(SO_4)_3,15H_2O$. L. J. S.

Measurements of the Radioactivity of Meteorites. TERENCE T. QUIRKE and LEO FINKELSTEIN (*Amer. J. Sci.*, 1917, [iv], **44**, 237—242).—The radium content of twenty-two meteorites not previously analysed was determined. The method of preparation consisted in dissolving the metallic part of the mineral in hydrochloric and nitric acid, and the undissolved part by fusion, separating the radium from the solution obtained by barium sulphate. The latter was fused with potassium–hydrogen sulphate in a test-tube, which was sealed. After the emanation had accumulated, the contents of the tube were again fused and air drawn through into the emanation electroscope. The results showed that the average stony meteorite contains less than a quarter of the radium in an average granite—$7\cdot6\times10^{-13}$ gram of radium per gram of meteorite for an average of seventeen—and that the metallic meteorites are almost free from radium. The meteorites examined included aërolites, chladnite, eukrites, chondrites, siderolites, iron meteorites, octahedrites, and hexahedrite. F. S.

Analytical Chemistry.

A Universal Gas-Volumeter. HORACE G. DEMING (*J. Amer. Chem. Soc.*, 1917, **39**, 2145—2151).—A direct reading gas-measuring apparatus is described, in which the volume of the gas collected is not only reduced mechanically to standard conditions, but converted automatically into the percentage of any desired constituent, no matter what the nature of the substance or weight of the sample submitted to analysis. H. M. D.

Use of Textile Fibres in Microscopic Qualitative Chemical Analysis. E. M. CHAMOT and H. I. COLE (*J. Ind. Eng. Chem.*, 1917, **9**, 969—971).—Silk fibres, previously treated with

10% sodium hydroxide solution for two hours at the ordinary temperature and then washed, are dyed with concentrated litmus solution, washed, treated with very dilute acetic acid solution or sodium hydroxide solution, and again washed. Fibres thus prepared form very sensitive indicators for the detection of acids or alkalis in minute drops of solution. In testing a drop of solution the fibre is so placed that a part of it is not moistened by the solution, and this part serves for comparison when the drop is observed under the microscope. A *N*/4500-solution of a mineral acid gives a distinct reaction with the fibres, but the reaction with alkalis is not quite so sensitive. The litmus used in preparing the fibres must be purified. Fibres dyed with Congo-red are useless for differentiating organic acids from mineral acids. W. P. S.

Influence of Added Substances on the End-point in the Iodometric Titration of Hydrogen Sulphide. ALFRED R. JAYSON and RALPH E. OESPER (*J. Ind. Eng. Chem.*, 1917, **9**, 975—977).—The red coloration which appears during the titration of hydrogen sulphide with iodine in acid solution is possibly due to acceleration of the hydrolysis of the starch to erythrodextrin under the conditions of the titration. This hydrolysis occurs at the point at which iodine and hydrogen sulphide react, and, although at ordinary concentrations iodine reacts with hydrogen sulphide and combines with starch in preference to erythrodextrin, at high local concentrations erythrodextrin iodide may also be formed. At the end of the titration, the mixture of red erythrodextrin iodide and blue starch iodide gives a purple coloration which changes to blue as the former compound decomposes. The addition of various salts (sodium chloride, calcium chloride, magnesium sulphate, etc.) does not make the end-point more definite.
W. P. S.

Estimation of Sulphur Dioxide [in Gases and Air]. O. R. SWEENEY, HARRY E. OUTCAULT, and JAMES R. WITHROW (*J. Ind. Eng. Chem.*, 1917, **9**, 949—950).—Oxidation with permanganate is recommended, since permanganate solution is more stable than is iodine solution. To ensure complete oxidation, the permanganate must always be present in excess. About 475 c.c. of water, 30 c.c. of 2*N*-sulphuric acid, and 10 c.c. of *N*/200-permanganate solution are placed in a stoppered bottle and about one-half of this mixture is transferred to another bottle; a small quantity of sulphurous acid is added to one portion so as nearly to destroy the pink colour, and permanganate solution is then added until the colour is equal to that of the solution in the other bottle; the solutions are again mixed and divided into two portions, one being reserved as a standard. (These operations are necessary owing to the fact that the colour obtained on re-titrating a mixture of sulphurous acid and permanganate is slightly different in tint from that of permanganate alone.) An excess of permanganate is then introduced into one of the bottles, this bottle is connected with the reservoir containing the sample of gas, the latter and the solution are mixed, and permanganate is then added until the coloration is equal to that of the comparison bottle. The quantity of permanganate solution used in these later operations is equivalent to the amount of sulphur dioxide present. W. P. S.

Estimation of Nitrogen by Kjeldahl's Method. OTTO NOLTE (*Zeitsch. anal. Chem.*, 1917, **56**, 391—393. Compare A., 1916, ii, 146).—In the case of caffeine and uric acid, the digestion with sulphuric acid is accelerated when a current of sulphur dioxide is passed through the mixture, but with tetramethylammonium hydrobromide, the decomposition is still incomplete. The addition of oxalic acid also favours the conversion of caffeine and uric acid into ammonia. W. P. S.

The Estimation of Nitrogen in Urine. MALTE LJUNGDAHL (*Biochem. Zeitsch.*, 1917, **83**, 115—119).—A modification of Kjeldahl's method adapted to small quantities of substance (for example, 1 c.c. of urine), in which the apparatus described by the author for the estimation of acetone (this vol., ii, 584) is employed for distilling off the ammonia. S. B. S.

Estimation of Ammonia in Soils. F. MÜNTER (*Landw. Versuchs-Stat.*, 1917, **90**, 147—189).—See this vol., i, 722).

A Method of Estimating Ammoniacal Nitrogen with Formaldehyde. G. H. C. VAN BERS (*Chem. Weekblad*, 1917, **14**, 968—975).—Formaldehyde reacts with ammonium salts in presence of excess of sodium hydroxide in accordance with the equation $6CH_2O + 2(NH_4)_2SO_4 + 4NaOH = C_6H_{12}N_4 + 2Na_2SO_4 + 10H_2O$. Titration of the excess of alkali furnishes the data required for calculating the percentage of ammonia, phenolphthalein being employed as indicator. Without the excess of alkali, free sulphuric acid is formed, but titration of the acid with alkali gives unsatisfactory results, owing to the end-point of the reaction being indefinite. A. J. W.

Some Factors influencing the Estimation of Nitric Nitrogen in the Soil. J. E. GREAVES and C. T. HIRST (*Soil Sci*, 1917, **4**, 179—205).—The following procedure is recommended for the estimation of nitrate nitrogen in soil. One hundred grams of the soil are shaken with 500 c.c. of water for five minutes, the solution being clarified either (1) by the addition of 2 grams of potassium alum with the soil, or (2) by filtering through a Chamberland-Pasteur filter, or (3) by centrifuging. If the estimation cannot be proceeded with at once, using methods (2) or (3), 0·5 c.c. of chloroform should be added to the solution. One hundred c.c. of the clear liquid is evaporated with 2 c.c. of strong aqueous sodium hydroxide down to 25 c.c., or, if carbamide is present, to dryness. The liquid is then diluted with 50 c.c. of water and reduced by Ulsch's method (compare A., 1891, 617, 960), using 5 grams of iron reduced by hydrogen and 30 c.c. of sulphuric acid (D 1·35), the estimation being completed in the usual manner. Provided that the soil is finely powdered, the five minutes' shaking is sufficient, and the proportion of soil to water may vary from 1 : 5 to 1 : 25. The chlorides, sulphates, or carbonates of sodium, potassium, calcium, magnesium, manganese, or iron do not interfere with Ulsch's method. W. G.

The Estimation of Soil Phosphorus. CLAYTON O. ROST (*Soil Sci.*, 1917, **4**, 295—311).—A comparison of six different methods for the estimation of the total phosphorus in a soil. The author has modified Washington's method for the estimation of phosphorus in rocks (compare "Manual of Chemical Analysis of Rocks," 1910) to make it equally satisfactory for soils. The modification consists in an ignition at a dull red heat prior to the treatment with hydrofluoric and nitric acids, and later taking up the phosphoric acid with nitric acid, and drying the residue in an air-bath at 110°. The amount of titanium oxide found in soils is too low to interfere with the precipitation of the phosphorus. W. G.

Estimation of Arsenic. III. Application to Iron Arsenic Pills. F. LEHMANN (*Arch. Pharm.*, 1917, **255**, 305—307).—The simplified method of estimating arsenic in animal material previously described (compare Ruff and Lehmann, A., 1912, ii, 866; Lehrmann, A., 1913, ii, 242) is now found to be applicable to vegetable material if the distillate containing the arsenic trichloride is collected, not in a solution of sodium hydrogen carbonate, but in 25% nitric acid; this solution is evaporated to dryness (whereby the volatile fission products of the organic matter which combine with iodine are oxidised), the residue is dissolved in a little alkali, and the arsenic acid in the filtered solution is estimated as usual after the addition of potassium iodide and sulphuric acid.

The application of the method to the estimation of the arsenic in iron arsenic pills is described in detail. C. S.

Testing Sulphuric Acid used in the Manufacture of Dextrose [for Arsenic]. ANDRÉ KLING (*Ann. Falsif.*, 1917, **10**, 451—453).—The Gutzeit test is recommended for the detection of arsenic in sulphuric acid, and a convenient form of apparatus is described for the purpose. W. P. S.

Arsenical Dextrose. ANDRÉ KLING (*Ann. Falsif.*, 1917, **10**, 438—450).—For the detection and estimation of arsenic in dextrose (commercial glucose), the Marsh, Gutzeit, and diaphanometric (turbidity obtained with sodium hypophosphite in sulphuric acid solution) methods are equally trustworthy. The last method, however, cannot be used if nitrates or nitrites are present. The arsenic in dextrose may be precipitated completely by treating the dextrose solution with bromine and then adding a small quantity of sodium phosphate and "magnesia mixture" and an excess of ammonia; the precipitate obtained is collected, washed, dissolved in nitric acid, the solution evaporated with the addition of sulphuric acid, and the residue tested in the Marsh apparatus. This procedure may be employed in place of the usual method of destroying the organic matter by heating with sulphuric acid and nitric acid. When arsenical dextrose is used in brewing, a small quantity (about one-tenth) of the arsenic present is "fixed" by the yeast when top fermentation yeast is employed; bottom fermentation yeast "fixes" only traces of the arsenic. W. P. S.

Estimation of Zinc by Schaffner's Method. G. FENNER and ROTHSCHILD (*Zeitsch. anal. Chem.*, 1917, **56**, 384—390. Compare A., 1916, ii, 578).—The necessity of having exactly the same amounts of zinc in the test solution and in the comparison solution applies only to the older modifications of the method. If hydrogen peroxide, potassium chlorate, or bromine is used to oxidise the iron present, care must be taken to remove the excess of these and certain reduction products before the titration is commenced. W. P. S.

Analysis of White Metal Alloys. Estimation of Lead, Copper, and Antimony. R. HOWDEN (*Chem. News*, 1917, **116**, 235).—For the estimation of lead and copper, the alloy (about 1 gram) is dissolved in a mixture of nitric and hydrochloric acids. Five c.c. of sulphuric acid and about 1 gram of tartaric acid are added to the solution, which is heated until the evolution of fumes ceases. The solution is then diluted and the precipitated lead sulphate filtered off. Sulphur dioxide is then passed into the filtrate, and the copper precipitated as cuprous iodide or as thiocyanate. The precipitate is dissolved in dilute nitric acid, and the copper estimated by the addition of potassium iodide and titration with sodium thiosulphate.

To estimate antimony, the alloy is dissolved in hydrochloric acid with the aid of potassium chlorate. Stannous chloride solution is added drop by drop until the yellow colour due to the copper is bleached, and the solution is then diluted and the copper reoxidised by passing air through the liquid. The antimony in the solution is then titrated by means of a standard solution of potassium bromate, the end-point being indicated by the addition of a little methyl-orange, which is bleached when the oxidation of the antimony is complete. H. M. D.

Use of Titanium Trichloride in Analytical Practice. F. MACH and P. LEDERLE (*Landw. Versuchs.-Stat.*, 1917, **90**, 191—224).—The use of titanium trichloride is recommended for various estimations, and when certain necessary precautions are taken, perfectly satisfactory results can be obtained. The authors suggest its use for the estimation of copper in copper sulphate and in the estimation of sugar by means of Fehling's solution, as well as for the examination of ferrous sulphate and hydrogen peroxide. The results obtained are as accurate as those given by gravimetric methods, and compare favourably with those of the permanganate method for the estimation of hydrogen peroxide. A convenient arrangement of the necessary apparatus is described. H. B. H.

Separation of Aluminium from Iron by means of Ether. Samuel Palkin (*J. Ind. Eng. Chem.*, 1917, **9**, 951—953).—The dried, mixed aluminium and ferric chlorides are treated with a small amount of absolute alcohol containing 30% of hydrogen chloride, and the mixture is evaporated until the salts crystallise. The residue is again moistened with acid alcohol containing a trace of water, and ether is added gradually. Hydrated aluminium chloride, of varying composition, is precipitated, whilst the ferric chloride remains in solution. W. P. S.

Estimation of Iron in Glass Sand. John B. Ferguson (*J. Ind. Eng. Chem.*, 1917, **9**, 941—943).—The sand must be decomposed completely before the iron content can be estimated. Treatment with hydrofluoric acid and sulphuric acid is not sufficient. The insoluble residue should be fused with potassium pyrosulphate, and a subsequent fusion with sodium carbonate is necessary in a few cases. W. P. S.

Estimation of Available Oxygen in Pyrolusite. O. L. Barneby (*J. Ind. Eng. Chem.*, 1917, **9**, 961—967. Compare this vol., ii, 274, 390).—The ferrous sulphate and direct iodometric methods are the most trustworthy for the estimation of available oxygen in pyrolusite. The oxalic acid method gives inaccurate results, owing to decomposition of the oxalic acid during the heating required for the solution of the ore; this decomposition is accelerated in sunlight and in the presence of manganese salts. A small quantity of carbon monoxide is evolved from dilute sulphuric acid solutions containing oxalic acid, but oxygen is not liberated when manganese dioxide and oxalic acid react in dilute sulphuric acid solution. W. P. S.

Examination of Light Petroleums and Benzenes. Jaroslav Formánek, Josef Knop, and Josef Korber (*Chem. Zeit.*, 1917, **41**, 713—714; 730—731).—The presence of benzene in light petroleums may be detected by shaking a portion of the sample with a small quantity of an aniline colour, such as "Blue BT" or "Violet RT," and filtering the mixture after two hours. If as little as 2% of benzene is present, the liquid will be coloured distinctly. By comparison with standards, this test may be rendered approximately quantitative. The presence of ether, alcohol, carbon disulphide, and chloroform interferes with the test to a certain extent. Tests for the detection of turpentine oil in light petroleum, depending on the absorption of bromine or iodine, are untrustworthy, since other unsaturated compounds are often present. The freezing point of a sample affords some indication of its composition. Pure benzene freezes at +5·5°; a mixture of 25% of benzene and 75% of toluene and xylene at −10° to −20°; a mixture of toluene and xylene at −70°; and technical xylene at −115°. The freezing point of light petroleum varies directly with the boiling point; a fraction boiling at 40° to 60° freezes at −198°, whilst a fraction boiling at 200° to 220° freezes at −93°.

W. P. S.

Table for the Analysis of Foods containing Sugar.

H. Lajoux and L. Ronnet (*Anal. Falsif.*, 1917, **10**, 453—457).—The following table is given as being useful to those engaged in the analysis of substances containing sugars. The solution, Σ, should be prepared from such a quantity of substance that it will contain from 5 to 10 grams of sugar per 100 c.c.; clarification is effected with basic lead acetate and sodium phosphate.

	In 100 c.c. of solution Σ.
Solution Σ: Q grams or V c.c. of sample per 100 c.c. Solution Σ inverted: Q grams or V c.c. of sample per 110 c.c. Dextrin solution: prepared from 100 c.c. of solution Σ. Fehling solution: 10 c.c. correspond with q gram of invert-sugar.	Sucrose, $S, = \frac{95\,D}{176{\cdot}75/0{\cdot}56t} = D \times K$. Reducing sugars, $R, = \frac{10{,}000q}{N \times V}$
Solution Σ: Polarisation in 20 cm. tube at $t° = A$. Polarisation of inverted solution in 22 cm. tube at $t° = A'$. $D = A - A'$.	Dextrose, $G, = \frac{50A + R(103{\cdot}4 - 0{\cdot}56t) - 66{\cdot}5S}{156{\cdot}4 - 0{\cdot}56t}$ If dextrin is present, A is replaced by $A - a$. Lævulose, $L, = R - G$.
Solution σ: 10 c.c. of Fehling solution reduced by N c.c.	Dextrose in excess, $g, = G - L$, or lævulose in excess, $l, = L - G$.
Dextrin solution: Polarisation in 20 cm. tube at $t° = a$. Reducing power of saccharified solution, 100/110. 10 c.c. of Fehling solution reduced by n c.c.	Invert-sugar, $I, = 2L$ or $2G$ according to which is the smaller. Dextrin, $\Delta, = \frac{99 \times q}{n}$

The dextrin solution (if dextrin is present) is obtained by evaporating 100 c.c. of solution Σ to a syrup, adding 3 c.c. of hydrochloric acid and 100 c.c. of 90% alcohol, and collecting the precipitate after three hours. The precipitate is then washed with alcohol, dissolved in hot water, reprecipitated as before, and dissolved in water to make 100 c.c. of solution. Saccharification is effected by boiling

50 c.c. of this solution for three hours with the addition of 0·5 c.c. of hydrochloric acid; after cooling, the solution is neutralised and diluted to 55 c.c. W. P. S.

Schneyer Method for the Estimation of Lactic Acid in Urine. MARY E. MAVER (*J. Biol. Chem.*, 1917, **32**, 71—76).—The modification of Meissner's method for the estimation of lactic acid described by Schneyer (A., 1915, ii, 804) gives results which are too high, owing to the formation of carbon monoxide from hippuric acid and other substances besides lactic acid in the urine. H. W. B.

Estimation of Lactic Acid in Wine by Möslinger's Method. THEODOR ROETTGEN (*Zeitsch. Nahr. Genussm.*, 1917, **34**, 198—207).—Mainly a reply to Baragiola and Schuppli (A., 1914, ii, 752). The barium chloride method as described originally (compare A., 1901, ii, 700; 1902, ii, 180; 1912, ii, 1005) is trustworthy, and, provided that allowance is made for loss of lactic acid during distillation and that the precipitation with alcohol in the proportion of 15:85 is carried out carefully, there is no need to modify the original process. W. P. S.

Estimation of Oxalic Acid in Food. E. ARBENZ (*Mitt. Lebensmittelunters. Hyg.*, **8**, 98—104; from *Chem. Zentr.*, 1917, ii, 320—321).—The oxalic acid content of foods is important in connexion with oxaluria. A table has been drawn up by Esbach for various foods. As doubt has been cast on some of the data, the author has carried out a series of analyses. The usual methods are either cumbersome or insufficiently accurate. The author recommends the following process. The dried material (10—20 grams) is heated under reflux on the water-bath with 15% hydrochloric acid (D 1·074, 150 c.c.), cooled, filtered into a measuring cylinder, and the residue lightly pressed. The clear, dark brown filtrate (120—140 c.c.) is exactly measured and evaporated to dryness. The residue is washed with water (about 20 c.c.) into an Allemann vessel and extracted with ether in a Soxhlet apparatus during twenty-four hours. After removal of the ether, the residue is dissolved in water, treated with ammonia, acidified with acetic acid, and the hot solution is precipitated with an excess of calcium chloride solution. After at least twelve hours, the precipitate is filtered, washed, redissolved in 6 c.c. of hydrochloric acid (15%), and again precipitated, and the process is repeated until the precipitate appears pure under the microscope. It is then ignited and weighed. The following data were thus obtained, the numbers representing grams of oxalic acid in 1000 grams (the figures in brackets are those given by Esbach): black tea, 14·3 (3·7); cocoa, 4·8 (4·5); pepper, 4·5 (3·2); rhubarb, 3·2 (2·4); spinach, 2·9 (3·2); sorrel, 2·7 (3·6); dried fig, 1·2 (1·0); roasted coffee, 0·8 (0·1); roasted chicory, 0·7 (0·7); wild strawberry, 0·6; raspberry, 0·5; bean, 0·45 (0·3); potato, 0·4 (0·4); beetroot, 0·3 (0·4); currant, 0·3;

pear, 0·45 (0·3); bilberry, 0·2; orange, 0·1; asparagus, 0·09 (?); cherry with stone, 0·08; tomato, 0·08 (0·05); grape, 0·08 (?); cabbage, 0·07; cauliflower, 0·06; onion, 0·05; scorzonera, 0·04; endive, 0·03 (0·01); melon, 0·03; mushroom, traces (?); peach, traces (?); meal, traces (0—0·17); lemon, traces (—); celery, traces (0·02); plum, traces (—); apple, traces (traces). Oxalic acid could not be detected in peas, maize meal, rice, or nuts. H. W.

Identification of Picric Acid in a case of Feigned Icterus. Simple Method of Identifying Poison in Blood. LÉON TIXIER (*Bull. Sci. Pharmacol.*, 1917, **24**, 155—159; from *Chem. Zentr.*, 1917, ii, 249).—The identification of picric acid is easily accomplished in the following manner. Fifteen drops of blood (taken from the finger tip) are mixed with 3 c.c. of sodium chloride solution (9·5%) and allowed to remain in an incubator for twenty-four hours. One to two c.c. of the salt solution are thoroughly agitated with an equal volume of methylene-blue solution (1:50,000), 10—15 drops of chloroform are added, and shaking is continued until any precipitate which may have been formed is again dissolved. After subsidence, a noticeable bottle-green to dark green coloration of the chloroform layer shows the presence of picric acid. The reaction is very sensitive and can be effected at a dilution of 1 part in 250,000. H. W.

The Estimation of Acetone. MALTE LJUNGDAHL (*Biochem. Zeitsch.*, 1917, **83**, 103—114).—The actone is distilled off in a current of steam in an apparatus of given dimensions. In the case of urine, 2—5 c.c. are used for analysis, according to the intensity of the Gerhardt reaction. The acetone which distils over is estimated iodometrically. S. B. S.

Colorimetric Estimation of Small Amounts of Aniline. ELIAS ELVOVE (*J. Ind. Eng. Chem.*, 1917, **9**, 953—955).—The method depends on the reaction between aniline and a hypochlorite, and is suitable for the estimation of aniline in the atmosphere of places where this substance is used; the aniline is obtained in solution by passing 10 litres of the air through 10 c.c. of very dilute sulphuric acid. According to the indications of a preliminary test, this solution is diluted, if necessary, so that it contains not more than 1 part of aniline in 200,000 parts of solution. Twenty c.c. of the solution are then mixed with 1 c.c. of calcium hypochlorite solution containing about 0·1% of available chlorine, and, after two minutes, 1 c.c. of $N/1$-sodium hydroxide solution is added. After a further ten minutes, the coloration obtained is compared with standards prepared with known amounts of aniline under the same conditions and at the same time. As little as 1 part of aniline in 2,000,000 parts of solution gives a reaction, but in this dilution the coloration obtained is yellow instead of purple. W. P. S.

INDEX OF AUTHORS' NAMES.

TRANSACTIONS AND ABSTRACTS.

1917.

(Marked T., and A., i and A., ii respectively.)

A.

Aáron, *B. von*, fate of caseinogen after intravenous injection, A., i, 717.

Aaslund, *Erling*. See *Hartwig* **Franzen**.

Abderhalden, *Emil*, and *Andor* **Fodor**, ferment action. I. The fermentative degradation of polypeptides, A., i, 306.

micro-Kjeldahl methods, A., ii, 540.

Abderhalden, *Emil*, and *Ernst* **Wybert**, synthesis of polypeptides, in the construction of which the amino-acids glycine, alanine, leucine, and cystine take part, A., i, 119.

Abelin, *Isak*, and *S.* **Lichtenstein-Rosenblat**, preparation of a bromo-derivative of *p*-aminophenyl salicylate, A., i, 454.

Abelin, *J.*, *p*-sulphomethylaminophenylarsinic acid, A., i, 487.

Abelous, *Jacques Emile*, and *Jules* **Aloy**, the biochemical phenomena of oxidoreduction, A., i, 618.

Absalom, *H. W. L.*, the ultra-violet transparency of certain coloured media, A., ii, 283.

Achterfeldt, *Friedr.* See *Max* **Busch**.

Ackroyd, *Harold*, and *Frederick Gowland* **Hopkins**, feeding experiments with deficiencies in the amino-acid supply; arginine and histidine as possible precursors of purines, A., i, 237.

Acree, *Solomon Farley*. See *Bessie M.* **Brown**, *W. A.* **Gruse**, *James McIntosh* **Johnson**, *Nathaniel Edward* **Loomis**, *Herbert A.* **Lubs**, *A. W.* **Mangam**, *Ernest J.* **Pieper**, *W. A.* **Taylor**, and *E. C.* **White**.

Adams, *Elliot Quincy*. See *George Augustus* **Linhart**, and *David R.* **Merrill**.

Adams, *H. S.*, thermal decomposition of the active principle of the pituitary gland, A., i, 526.

Adams, *J. R.* See *George Leslie* **Kelley**.

Adams, *Roger*, and *C. H.* **Beebe**, action of the Grignard reagent on cyanogen compounds; synthesis of amidines from cyanamides, A., i, 96.

Adams, *Roger*, and *L. F.* **Weeks**, action of oxalyl chloride on primary, secondary, and tertiary alcohols, A., i, 4.

Adanti, *Guido*, volumetric estimation of zinc phenolsulphonate, A., ii, 517.

Addis, *Thomas*, and *C. K.* **Watanabe**, method for the measurement of the urea-excreting function of the kidneys, A., i, 103.

rate of excretion of urea. III. Effect of changes in the concentration of urea in the blood on the rate of excretion of urea. IV. Effect of changes in the volume of urine on the rate of excretion of urea, A., i, 367.

Addis, *Thomas*. See also *George D.* **Barnett**.

Adler, *Ludwig*, the influence of the hydrion concentration on the activity of malt diastase, A., i, 61.

the boric acid method of estimating ammonia, A., ii, 40.

Adolph, *Edward F.* See *D. Wright* **Wilson**.

Aktien Gesellschaft für Anilinfabrikation, preparation of 3-nitrocarbazole and its halogen derivatives, A., i, 475.

Alber, *A.* See *Rudolf Friedrich* **Weinland**.

Albertson, *J. M.* See *Percy Norton* **Evans**.

Albright, *Alan R.*, a method for the examination of methyl salicylate, A., ii, 279.

Aldrich, *Thomas Bailey*, and *C. P.* **Beckwith**, derivatives of trihalogeno-*tert.*-butyl alcohols. I. The acetic ester of tribromo-*tert.*-butyl alcohol or brometone acetic ester, A., i, 77.
Alexander, *Jerome*, selective adsorption and differential diffusion, A., ii, 242.
Algar, *Joseph*, unsaturated ketones derived from diacetylorcinol, A., i, 345.
Allan, *John A.* See *Charles H.* **Warren.**
Allen, *C. H.* See *Phœbus A.* **Levene.**
Allen, *Eugene Thomas*, and *Robert H.* **Lombard**, a method for the determination of dissociation pressures of sulphides and its application to covellite (CuS) and pyrites (FeS_2), A., ii, 194.
Allen, *Eugene Thomas.* See also *Emanuel George* **Zies.**
Allen, *H. C.* See *William Ridgely* **Orndorff.**
Allison, *F. E.*, biological changes in soil during storage, A., i, 243.
Allison, *F. E.*, and *R. C.* **Cook**, the effect of ammonium sulphate on soil acidity, A., i, 621.
Allison, *F. E.* See also *R. C.* **Cook.**
Almström, *G. Karl*, microchemical analysis of explosive substances, A., ii, 541.
Aloy, *Jules.* See *Jacques Emile* **Abelous.**
Alway, *Frederick Jacob*, and *Guy R.* **McDole**, relation of the water-retaining capacity of a soil to its hygroscopic coefficient, A., i, 509.
Amann, *J.*, estimation of polypeptides and amino-acids in blood, A., ii, 54.
Aminoff, *G.*, crystallographical and optical observations on some organic compounds, A., i, 143.
Anderegg, *Frederick Osband.* See *Theodore William* **Richards.**
Andersen, *Erik Buch*, catalytic oxidation of ammonia, A., ii, 138.
Anderson, *George W.*, detection of hydrocyanic acid, A., ii, 182.
Anderson, *H. S.* See *John Matthew* **Wilkie.**
Anderson, *O. H.* See *R. H.* **Carr.**
Anderson, *Ross P.*, reagents for use in gas analysis. V. The relative advantages of the use of sodium and potassium hydroxides in the preparation of alkaline pyrogallol, A., ii, 39.
  the estimation of gasolene vapour in air, A., ii, 338.
Andersson, *Erik*, relation between the physical properties of solutions and their mixtures, A., ii, 126.
Andreasch, *Rudolf*, substituted rhodanines and some of their aldehyde condensation products. XIII., A., i, 663.
Andreev, *N.*, processes of adsorption in chemotherapeutics and immunity, A., i, 183.
Andrén, *L.*, computation and measurement of the complex molecules of certain vapours according to the new condensation theory, A., ii, 192.
Andrews, *C. E.* See *R. S.* **Boehner.**
Andrlík, *Karl*, does the addition of sulphuric acid to the soil affect the growth of the beet? A., i, 620.
Angel, *Andrea*, obituary notice of, T., 321.
Angeli, *Angelo*, azocarboxylic acids, A., i, 228.
  oxidation of phenylazocarbonamide, A., i, 417.
  analogies between derivatives of oxygen and those of nitrogen. II., A., i, 452.
Angeli, *Angelo*, and *Guido* **Cusmano**, nitrosopyrrole-black, A., i, 413.
Angeli, *B.*, new laboratory apparatus for the evolution of gas, A., ii, 173.
Angiolani, *A.*, quantitative test for uric acid in urine, A., ii, 429.
Annett, *Harold Edward*, raffinose in the seed of the jute plant (*Corchorus capsularis*), A., i, 506.
Anselmino, *Otto*, the *m*-homosalicylaldehydes and their derivatives, A., i, 342.
Anslow, *Gladys A.*, and *Janet T.* **Howell**, the triplet series of radium, A., ii, 401.
Anwandter, *R.* See *Leo* **Ubbelohde.**
Appelius, *W.*, and *R.* **Schmidt**, estimation of basicity of chromium extracts and infusions, A., ii, 44.
Arbenz, *E.*, estimation of oxalic acid in food, A., ii, 583.
Archibald, *Ebenezer Henry*, and *Y.* **Habasian**, the solubility of aluminium hydroxide in solutions of ammonia and ammonium salts, A., ii, 93.
Archibald, *Ebenezer Henry*, and *H. B.* **Keegan**, the occlusion of iron by the ammonium phosphomolybdate precipitate, A., ii, 95.
Ariès, *E.*, the tension of saturated vapour at low temperatures and the chemical constant, A., ii, 192.
Arkuszewski, *Z.* See *Julius von* **Braun.**
Arnd, *Th.*, estimation of nitrogen in nitrates and nitrites, A., ii, 504.
Arnold, *Hans*, the structure of metallic coatings prepared by the metallic spraying method, A., ii, 260.
Arnold, *K.* See *Theodor* **Zincke.**

Arrhenius, *Svante* [*August*], viscosity and hydration of colloidal solutions, A., ii, 130.

viscosity of solutions, A., ii, 443.

Arsdel, *W. B. van*. See *Hugh K.* **Moore.**

Artini, *Ettore*, polymorphism of 2:6-dinitro-4-toluidine. I. and II., A., i, 389.

the crystalline form of some benzene derivatives, A., i, 553.

Artom, *Camillo*, metabolism of dextrose in surviving organs. II. Action of the pancreas on dextrose circulating in it, A., i, 186.

metabolism of dextrose in surviving organs. III. Action of the spleen on dextrose circulating in it, A., i, 186.

Asch, *D*. See *W.* **Asch.**

Asch, *W.*, and *D.* **Asch**, topic parameters in the light of the stereo-hexite-pentite theory, A., ii, 449.

the constitution of some minerals of the mica group in the light of the stereo-hexite-pentite theory, A., ii, 494.

Aschkenasi, *S.*, production of per-salts (perphosphates and perarsenates), A., ii, 467.

production of anhydrous per-salts or mixtures of per-salts, A., ii, 468.

Aschman, *C., jun.*, estimation of boron in boron-steel, A., ii, 102.

Askenstedt, *F. C.*, improved test for indican in urine, A., ii, 553.

Aston, *James*, the effect of rust on the corrosion of iron and steel, A., ii, 191.

Astruc, *A.*, piperazine cacodylate, A., i, 9.

calcined magnesia, A., ii, 508.

Aten, *Adriaan Hendrik Willem*, some particular cases of current-potential lines, A., ii, 163, 190.

theory of the electrolytic estimation of the halogens as silver haloids, A., ii, 419.

Aten, *Adriaan Hendrik Willem*. See also *Andreas* **Smits.**

Atkins, *William Ringrose Gelston*, application of the method of constant boiling-point mixtures to the qualitative analysis of certain mixed organic liquids, A., ii, 47.

analysis of honey and other substances containing lævulose, A., ii, 157.

Aubry, *A.*, influence of alcohol concentration and temperature on the biochemical synthesis of α-methylgalactoside, A., i, 72.

Aubry, *A*. See also *Émile* **Bourquelot.**

Auffenberg, *Elisabeth*. See *Karl von* **Auwers.**

Aufhäuser *David*. See *Theodor* **Curtius.**

Aufrecht, *Arthur*, detection of albumin in urine, A., ii, 227.

Aurén, *Tycho E:son*, absorption of X-rays, A., ii, 350.

Aust, *E*. See *Julius von* **Braun.**

Autenrieth, *Wilhelm*, colorimetric estimation of serum-albumin and globulin in urine, ascitic fluid, and blood serum, A., ii, 400.

Auwers, *Karl von*, the hydroaromatic ketones obtained from phenols and chloroform, and their transformations, A., i, 34.

spectrochemistry of benzene derivatives; cinnamic esters; hydroxystyrenes and their ethers, A., i, 266.

1:1:4.trimethylcoumaranone and 3:6-dimethylchromanone (3:6-dimethyl-1:4-benzopyrone), A., i, 277.

preparation of α-benzildioxime, A., i, 572.

spectrochemistry of benzene derivatives and cinnamic esters, A., ii, 188.

Auwers, *Karl von*, and *Elisabeth* **Auffenberg**, constitution of mono- and di-acylmalonic esters, and of diacetylacetone, A., i, 627.

Auwers, *Karl von*, and *E.* **Hilliger**, 5- and 7-hydroxyhydrindones, A., i, 37.

Averitt, *S. D.*, the estimation of strontium and lithium in water, A., ii, 423.

Aylsworth, *A. M.* See *J. W.* **Aylsworth.**

Aylsworth, *J. W.*, *A. M.* **Aylsworth**, and **The Savings, Investments, and Trusts Co., Exors.**, preparation of phenol and other substances, A., i, 331.

B.

Baat, (*Miss*) *Woutrine Constance de*. See *Frans Antoon Hubert* **Schreinemakers.**

Babcock, *Henry A*. See *Frederick G.* **Keyes.**

Bach, *Alexis*, non-specificity of the animal and vegetable reducing ferment, A., i, 375.

the reducing ferments, A., i, 431.

Bachmann, *Wilhelm*, the Prussian blue hydrosol, A., i, 688.

vapour-pressure isotherms of substances with gel structure, A., ii, 562.

Backman, *E. L.*, olfactology of the methylbenzene series, A., i, 498.

Badische Anilin- & Soda-Fabrik, preparation of β-chloro*iso*pentane, A., i, 77.

Badische Anilin- & Soda-Fabrik, preparation of aromatic amines and catalysts therefor, A., i, 127.
  preparation of *o*-chlorotoluene, A., i, 258.
  preparation of acetic acid from acetaldehyde, A., i, 377.
  hydrogenisation and dehydrogenisation of carbon compounds, A., i, 377.
Bado, *Atilio A.*, action of copper sulphate on the algæ of potable water, A., i, 107.
  estimation of organic carbon in water, A., ii, 541.
Bäck, *Thekla*, replacement of acetic acid in chemical investigations, A., ii, 520.
Baerwind, *Ernst.* See *Franz* **Fischer.**
Bässler, *Edmund.* See *Rudolf Friedrich* **Weinland.**
Bagster, *Lancelot Salisbury*, compounds of calcium chloride and acetone, T., 494 ; A., i, 443.
Bailey, *George C.* See *Treat Baldwin* **Johnson.**
Bailey, *James R.*, and *A. T.* **McPherson**, the 2-thio-3-aryl-5:5-dimethylhydantoins, A., i, 54.
  the criss-cross addition on conjugate systems; the action of cyanic acid, thiocyanic acid, and *iso*cyanates of azines, A., i, 587.
Bailey, *James R.*, and *N. H.* **Moore**, the use of cyanic acid in glacial acetic acid. II. The addition of cyanic acid to benzaldazine, A., i, 355.
Bailly, *Octave*, the constitution of the phosphoric esters of glycerol, A., i, 2.
  does the law of mass action regulate diastatic reactions ? A., ii, 457.
Bain, *James Watson*, and *C. E.* **Oliver**, the double salts formed by sodium and potassium carbonates, A., ii, 87.
Baker, *G. Burton*, wasahba wood, A., i, 682.
Baker, *Julian Levett*, and *Henry Francis Everard* **Hulton**, evidence of the existence in malt of an enzyme hydrolysing the furfuroids of barley, T., 121 ; A., i, 310.
Baker, *Ross Allen*, laboratory experiment ; enrichment of illuminating gas, A., ii, 255.
Bakker, *Gerrit*, the Kamerlingh Onnes equation of condition and the theory of the capillary layer, A., ii, 16.
Balareff, *D.*, the action of phosphoryl chloride on methyl or ethyl alcohol, A., i, 625.
  the velocity of hydration of metaphosphoric acid. II., A., ii, 23.
  the molecular weight of ortho- and pyro-phosphoric acid, A., ii, 85.
Balareff, *D.*, the dehydration of sodium hydrogen phosphate, A., ii, 88.
  the colour of magnesium pyrophosphate obtained by calcining $MgNH_4PO_4,6H_2O$, A., ii, 90.
  the acidimetric estimation of orthophosphoric acid, A., ii, 101.
  the structure of pyrophosphoric acid, A., ii, 467.
  volumetric estimation of pyrophosphoric acid, A., ii, 506.
Balcom, *Reuben Wilfrid*, the volatile reducing substance in cider vinegar, A., i, 313.
Baldes, *Karl*, and *Fritz* **Silberstein**, synthetic sugar formation in the artificially perfused liver. II., A., i, 673.
Balduzzi, *O.* See *Mario* **Raffo.**
Balke, *Clarence William.* See *Edgar W.* **Engle**, and *B. Smith* **Hopkins.**
Ball, *Alice A.* See *William Maurice* **Dehn.**
Ball, *T. R.* See *George McPhail* **Smith.**
Ball, *Walter Craven.* See *Charles George Lewis* **Wolf.**
Bancroft, *Wilder Dwight*, theory of peptisation, A., ii, 129.
  liquid films in capillary tubes, A., ii, 362.
  semipermeable membranes and negative adsorption, A., ii, 444.
  contact catalysis. I., A., ii, 566.
Banta, *Clifford.* See *John Bernard* **Ekeley.**
Barab, *Jacob.* See *W. C.* **Cope**, and *Marks* **Neidle.**
Baragiola, *W. I.*, the white turbidity of wines, A., i, 620.
Baragiola, *W. I.*, and *Ch.* **Godet**, analytical differentiation between fermented sweet wines and "mistelles," A., ii, 156.
Baragiola, *W. I.*, and *O.* **Schuppli**, estimation of ammonia in the soil and in liquid manure, A., ii, 380.
Barbieri, *Nicola Alberto*, non-existence of free or combined lecithin in egg-yolk and in animal and vegetable biological structures, A., i, 238.
  criticism of the use of superphosphates in agriculture, A., i, 312.
Barger, *George*, and *Arthur James* **Ewins**, synthesis of *r*-2-methyltryptophan, A., i, 476.
Barker, *J. F.*, estimation of carbonates in limestone and other materials, A., ii, 506.
Barker, *M. F.* See *John Jacob* **Fox.**
Barnebey, *O. L.*, differential iodometry. II. The titration of chromic acid in the presence of ferric iron and the analysis of chromite for its chromium content, A., ii, 274.

Barnebey, *O. L.*, estimation of available oxygen in pyrolusite, A., ii, 581.

Barnebey, *O. L.*, and *Geo. M.* **Bishop**, differential iodometry. IV. The analysis of pyrolusite and other oxidised manganese ores, A., ii, 390.

Barnebey, *O. L.*, and *W. C.* **Hawes**, differential iodometry. III. Estimation of the available oxygen in soluble and precipitated oxidised forms of manganese, A., ii, 274.

Barnett, *George D.*, micro-titration of ammonia, with some observations on normal human blood, A., i, 359.

Barnett, *George D.*, and *Thomas* **Addis**, urea as a source of the ammonia in the blood, A., i, 491.

Bartell, *F. E.*, direct reading ionometer, A., ii, 235.

Bassett, *Henry, jun.*, the phosphates of calcium. IV. The basic phosphates, T., 620; A., ii, 413.

Bateman, *W. G.*, and *Lansing S.* **Wells**, copper in the flora of a copper-tailing region, A., i, 373.

Batuecas, *T.*, electroanalysis of tin without platinum electrodes, A., ii, 106.

Bau, *Arminius*, the constitution of amygdalin, A., i, 407.

Baudisch, *Oskar*, nitrosoarylhydroxylamines. VII. Hydroxyazoxy-compounds and nitrosophenylhydroxylamines, A., i, 356.
  nitrate and nitrite assimilation. XII., A., i, 434.
  theory of colour lakes, A., i, 556.

Baudisch, *Oskar*, and *Rose* **Fürst**, nitrosoarylhydroxylamines. V. Internally complex metallic salts., A., i, 330.

Baudisch, *Oskar*, and *J.* **Haftka**, 2:2′-dihydroxyazoxybenzene, A., i, 357.

Baudisch, *Oskar*, and *Arthur Baron* **Hoschek**, auto-oxidation of indoles in daylight, A., i, 166.

Baudisch, *Oskar*, and *Nikolaus* **Karzeff**, nitrosoarylhydroxylamines. VI. Internally complex metallic salts, A., i, 330.

Baudisch, *Oskar*, and *Franz* **Klaus**, nitrosoarylhydroxylamines. VII. Internally complex metallic salts; note on mordant dyes, A., i, 331.

Baudoux, *L.* See *Charles* **Dhéré**.

Bauer, *Constanze*. See *Otto* **Fischer**.

Bauer, *H.* See *G.* **Ramann**.

Bauermeister, *Martin*. See *Wilhelm* **Steinkopf**.

Baumann, *C.*, and *Johannes* **Grossfeld**, polarimetric estimation of starch in the presence of other optically active substances, A., ii, 223.

Baumann, *Louis*, and *H. M.* **Hines**, origin of creatine. II., A., i, 677.

Baume, *G.* See *Louis* **Lutz**.

Baur, *Emil*, and *S.* **Kronmann**, ion adsorption potentials, A., ii, 231.

Baur, *Emil*, *Agnes* **Petersen**, and *G.* **Füllemann**, fuel cells at high temperatures, A., ii, 116.

Bauzil and **Boyer**, estimation of dextrose in blood, A., ii, 548.

Baxter, *Gregory Paul*, Twenty-fourth Annual Report of the Committee on Atomic Weights; determinations published during 1916, A., ii, 254.

Baxter, *Gregory Paul*, and *Matsusuke* **Kobayashi**, the estimation of potassium as perchlorate, A., ii, 270.

Bazzoni, *Charles Blizard*, experimental determination of the ionisation potential of helium, A., ii, 63.

Bazzoni, *Charles Blizard*. See also *Owen Willans* **Richardson**.

Beal, *George Denton*, and *Fred Weaver* **Muncie**, effects of large applications of commercial fertilisers on carnations, A., i, 190.

Beal, *George Denton*, and *Ruth* **Okey**, the qualitative identification of the drugs containing emodin, A., ii, 279.

Beckenkamp, *J.*, crystal structure and chemical valency, A., ii, 296.

Becker, *H.* See *Hermann* **Staudinger**.

Beckett, *E. G.*, a laboratory gas meter, A., ii, 137.

Beckmann, *Ernst*, *Otto* **Liesche**, and *Werner* **Gabel**, the molecular condition of acetic acid in boiling benzene and in the saturated vapour from the solution, A., ii, 564.

Beckwith, *C. P.* See *Thomas Bailey* **Aldrich**.

Bedford, *Clayton W.*, production of the lower chlorides of methane from natural gas, A., i, 77.

Bedford, *Clayton W.* See also *William Roy* **Mott**.

Beebe, *C. H.* See *Roger* **Adams**.

Behrman, *A. S.*, the Blacher method for the estimation of hardness in water, A., ii, 542.

Beketov, *N. N.* See *Nicolai S.* **Kurnakov**.

Bell, *James Munsie*, free energy and heat capacity, A., ii, 65.

Bell, *James Munsie*. See also *Francis P.* **Venable**.

Bell, *Richard D.* See *Otto* **Folin**.

Benary, *Erich*, *Fritz* **Reiter**, and *Helene* **Soenderop**, acylation of ethyl β-aminocrotonate and analogous compounds. II., A., i, 252.

Bencker, *F.* See *Ernst Hermann* **Riesenfeld.**
Benda, *Ludwig*, arsenic compounds of the anthraquinone group, A., i, 599.
Benger, *Ernest Baden*, reduction of selenic acid, A., ii, 568.
  reduction of telluric acid, A., ii, 569.
Bengis, *Robert.* See *William* **Salant.**
Bennett, *Charles W.*, and *W. S.* **Burnham,** the passive state of metals, A., ii, 209.
Bennett, *Charles W.*, and *E. L.* **Mack,** electrolytic formation of perchlorate, A., ii, 199.
Bennett, *George Macdonald*, the crystal form and isomerism of some ferrocyanides, T., 490; A., i, 449.
Benrath, *Alfred*, cupric cuprous sodium thiosulphate ammoniate, A., ii, 260.
Benton, *T. H.* See *Ralph S.* **Potter.**
Berczeller, *L.*, the surface tension of stereoisomeric compounds, A., ii, 442.
Berg, *Ragnar*, estimation of small quantities of iron and aluminium, A., ii, 220.
Berg, *William N.*, transformation of ψ-globulin into euglobulin, A., i, 485.
Bergeim, *Olaf.* See *C. C.* **Fowler.**
Bergell, *Peter*, compounds of amino-acids and ammonia. IX., A., i, 448.
Berger. See *Max* **Cremer.**
Bergh, *A. A. Hymans van den*, and *P.* **Muller,** a direct and indirect diazo-reaction for bilirubin, A., ii, 58.
Bergius, *Margarete.* See *Heinrich* **Biltz.**
Bergmann, *Max.* See *Emil* **Fischer.**
Berner, *E.* See *Claus Nissen* **Riiber.**
Bernthsen-Buchner, *Daisy.* See *Adolf* **Windaus.**
Bers, *G. H. C. van*, a method of estimating ammoniacal nitrogen with formaldehyde, A., ii, 578.
Bertele, *F.* See *Ludwig* **Vanino.**
Berthelot, *Albert*, the production of phenol by bacteria, A., i, 305.
Berthoud, *A.*, determination of the critical temperatures and pressures of alkylamines and alkyl chlorides, A., ii, 237.
Bertsch, *A.* See *Johannes* **D'Ans.**
Besson, *A. A.*, detection of small quantities of oxalic acid in wine, A., ii, 516.
Beutel, *Ernst*, influence of light on the loss of water of crystallisation from salts, A., ii, 63.
Bezzenberger, *F. K.*, hydrogen sulphide generator, A., ii, 368.
  a titration flask, A., ii, 499.
Biberfeld, *Johannes*, tolerance to morphine. II. The specificity of the tolerance, A., i, 106.
Bichowsky, *F. Russell von*, electrometric titration of zinc with ferrocyanide, A., ii, 219.
Biddle, *Henry Chalmers*, and *Thomas* **Watson,** the influence of varying concentration of hydrogen ion on the optical rotation of the isomeric alkaloids, cinchonine, cinchonidine, and cinchotoxine, A., i, 471.
Biedermann, *W.*, studies in fermentation. II. Autolysis of starch, A., i, 62.
Biehler, *Ferd.* See *Carl* **Paal.**
Bigelow, *Samuel Lawrence*, and *Edward A.* **Rykenboer,** capillary phenomena and supercooling, A., ii, 444.
Biilmann, *Einar*, the formation and decomposition of some organic halogenated compounds, A., i, 378.
Biilmann, *Einar*, and *Johanne* **Bjerrum,** the isomeric 3-methyluric acids, A., i, 177.
  investigations in the cyanic acid series, A., i, 382.
  methyl- and ethyl-uric acids, A., i, 588.
Biilmann, *Einar*, and (*Mlle.*) *Agnes* **Hoff,** the complexity of some organic compounds of mercury, A., i, 123.
  some complex compounds of platinum and mercury, A., i, 123.
Bilecki, *Alois*, fundamental atomic weights, A., ii, 197.
Bilhuber, *Ernst A.* See *Wilhelm* **Wislicenus.**
Billows, *E.*, analyses of Venetian minerals, A., ii, 492.
Biltz, *Heinrich*, [uric acid derivatives], A., i, 286.
Biltz, *Heinrich*, and *Margarete* **Bergius,** derivatives of trimethyl-9-ethyluric acid, A., i, 589.
Biltz, *Heinrich*, and *Paul* **Damm,** derivatives of 1:7-dimethyluric acid, A., i, 294.
  derivatives of 3:7:9-trimethyluric acid, A., i, 298.
Biltz, *Heinrich*, and *Myron* **Heyn,** derivatives of uric acid, A., i, 286.
  preparation of alloxan, A., i, 289.
  derivatives of 9-methyluric acid, A., i, 291.
  α-, ζ-, and δ-methyluric acids, A., i, 292.
  derivatives of 1:3:7-trimethyluric acid, A., i, 298.
Biltz, *Heinrich*, *Myron* **Heyn,** and *Margarete* **Bergius,** alloxanic acid, A., i, 289.
  *spiro*hydantoins, A., i, 290.
Biltz, *Heinrich*, and *Fritz* **Max,** trimethyl-1-ethyluric acid and its derivatives, A., i, 589.

Biltz, *Heinrich*, and *Fritz* **Max**, 3:7-dimethyl-1:9-diethyluric acid and its derivatives, A., i, 590.
derivatives and degradation of 3:7-dimethyl-1-ethyluric acid, A., i, 590.
Biltz, *Heinrich*, and *Karl* **Strufe**, derivatives of 1-methyluric acid, A., i, 293.
derivatives of 1:3-dimethyluric acid, A., i, 296.
derivatives of 1:3:7:9-tetramethyluric acid, A., i, 299.
Biltz, *Wilhelm*, *Günther* **Bugge**, and *Ludwig* **Mehler**, osmotic pressure of colloids. VI. Osmotic pressure of gelatin, A., ii, 17.
Binger, *Carl*, toxicity of phosphates in relation to the calcium in the blood and to tetanus, A., i, 677.
Binggely, *Ch.* See *J.* **Kliatchko.**
Bishop, *Geo. M.* See *O. L.* **Barnebey.**
Bissell, *D. W.* See *Clarence G.* **Derick.**
Bjerrum, *Johanne.* See *Einar* **Biilmann.**
Bjerrum, *Niels*, modern views of acid and alkaline reactions and their application to analysis. I. and II., A., ii, 215.
Blackman, *Philip*, a new method for the determination of vapour densities. X., A., ii, 68.
Blake, *John Charles*, the digestibility of bread. II. Salivary digestion of erythrodextrin in vitro, A., i, 361.
Blanc, *Lucrecia M.*, refractometry of solutions, A., ii, 229.
Blanck, *Edwin*, the significance of sodium salts for plant growth and the application of salt as manure, A., i, 624.
Bloch, *Br.*, specific pigment-forming ferment of the skin, dopaoxydase, A., i, 675.
Bloch, *M. A.* See *Michael A.* **Rakuzin.**
Bloor, *W. R.*, estimation of cholesterol in blood, A., ii, 275.
Bloor, *W. R.*, and *Arthur* **Knudson**, cholesterol and cholesterol esters in human blood, A., i, 236.
Bloor, *W. R.*, and *D. J.* **MacPherson**, blood lipoids in anæmia, A., i, 609.
Blount, *Bertram*, the limitations of the balance, T., 1035.
Blumenthal, *Philip Lee*, *A. M.* **Peter**, *D. J.* **Healy**, and *E. J.* **Gott**, method of ashing organic materials for the estimation of potassium, A., ii, 507.
Blunt, *Katharine*, and *Chi Che* **Wang**, Chinese preserved eggs; Pidan, A., i, 102.
Boas, *Friedrich*, the formation of starch by moulds, A., i, 370.
the formation of starch-like substances by moulds, A., i, 503.
Bock, *Joseph C.*, amino-acid nitrogen content of the blood of various species, A., i, 360.
estimation of amino-nitrogen in blood, A., ii, 159.
Bock, *Laurenz*, zinc chromates and their significance for the colour industry, A., ii, 312.
constitutional relation of ultramarines with other silicates, A., ii, 475.
Bocquillon, *H.*, new active principles in the genus *Xanthoxyllum*, A., i, 276.
Bodenstein, *Max*, and **Schubart**, physico-chemical foundations of the commercial zinc extraction, A., ii, 312.
Bodforss, *Sven*, aromatic oxido-compounds [ethylene oxides], A., i, 223.
Bœdtker, *Eyvind*, and *O. M.* **Halse**, the Friedel-Crafts' reaction, A., i, 124.
Böggild, *O. B.*, dahllite from Kangerdluarsuk, Greenland, A., ii, 145.
Böggild, *O. B.*, and *C.* **Christensen**, leifite, a new mineral from Narsarsuk, Greenland, A., ii, 147.
Boehner, *R. S.*, and *C. E.* **Andrews**, the pyrogenetic decomposition of amides. I., A., i, 10.
Boehner, *R. S.*, and *A. L.* **Ward**, the pyrogenetic decomposition of amides. II., A., i, 11.
Boeke, *Hendrik Enno*, the system anorthite–forsterite–silica, A., ii, 147.
an application of polydimensional geometry to chemico-mineralogical problems; the composition of tourmaline, A., ii, 178.
four-component systems, A., ii, 195.
Boekhout, *Fritz Willem Jacob*, and *J. J. Ott de* **Vries**, Duclaux's method for the estimation of volatile fatty acids, A., ii, 50.
Boer, *S. de*, influence of respiration on the exchange of SO_4 between corpuscles and plasma, and its effect on the excretion of SO_4, A., i, 671.
Boericke, *F.*, convenient filtration apparatus for the estimation of sugar by titration of the cuprous oxide precipitated from Fehling's solution, A., ii, 547.
Börner, *Kurt.* See *Wilhelm* **Wislicenus.**
Böttcher, *Bruno.* See *Paul* **Rabe.**
Bogert, *L. Jean*, modifications of the colorimetric estimation of uric acid in urine and in blood, A., ii, 518.
Bogitch, *B.* See *Henri* **Le Chatelier.**
Bogitch, *F.* See *Henri* **Le Chatelier.**
Bohn, *Ralph M.*, iodine content of food materials, A., i, 192.
Bohnson, *Van L.* See *Joseph Howard* **Mathews.**

Boiteau, *Georges*, manufacture of esters, A., i, 2.

Bokhorst, *S. C.* See *Andreas* **Smits**.

Bokorny, *Thomas*, formation of albumin from different sources of carbon, A., i, 72.
the increase of dry weight of yeast when urea is used as the source of nitrogen, A., i, 680.
relationship between sugar fermentation and sugar-assimilation, A., i, 681.
benzene derivatives as sources of nourishment, A., i, 682.
chemistry of nutrition, A., i, 718.

Bolton, *Elmer Keiser*. See *Richard* **Willstätter**.

Boncquet, *Mary*. See *P. A.* **Boncquet**.

Boncquet, *P. A.*, presence of nitrites and ammonia in diseased plants; its significance with regard to crop rotation and soil depletion, A., i, 74.

Boncquet, *P. A.*, and *Mary* **Boncquet**, presence of nitrites and ammonia in diseased plants. I. Oxydases and diastases; their relation to the disturbance, A., i, 683.

Bonis, *A.*, the practical methods for the detection and estimation of "saccharin" in foodstuffs, A., ii, 430.

Bonnerot, *S.* See *Georges* **Charpy**.

Booth, *Harold S.* See *Albert F. O.* **Germann**.

Bordier, *H.*, and *G.* **Roy**, colloidal iodine, A., ii, 29.

Bornwater, *Johan Theodorus*, the action of oxalyl chloride on some amino-compounds, A., i, 121.
some derivatives of amino-acids, A., i, 137.

Borrien, *V.*, uroerythrin, A., i, 577.

Borsche, *Walther*, constitution of meconic acid, A., i, 117.
3:3′-diphenol, A., i, 558.

Borsche, *Walther*, and *B. G. B.* **Scholten**, some new derivatives of diphenyl, A., i, 390.

Borsche, *Walther*, *L.* **Stackmann**, and *J.* **Makaroff-Semljanski**, mononitrohalogenobenzenes with mobile halogen, A., i, 15.

Boruttau, *Heinrich*, how are the plant proteins of the diet utilised in the animal body? II., A., i, 605.

Bosworth, *Alfred W.*, and *H. I.* **Bowditch**, infant feeding; the chemical changes produced by the addition of calcium hydroxide to milk, A., i, 184.

Bottomley, *William Beecroft*, the isolation from peat of certain nucleic acid derivatives, A., i, 724.

Boudet, *Jean*. See *Paul* **Nicolardot**.

Bougault, *J.*, semicarbazones of α-ketonic acids; *αα*-di-iodo- and di-bromophenylbutyric acids; α-iodo- and α-bromophenylcrotonic acids, A., i, 26.
mixed anhydrides derived from benzoylacrylic acid, A., i, 270.
isomerisation, by migration of the double linking, in the ethylenic acids; phenyl-Δ^{α}-crotonic acid, $CH_2Ph\cdot CH:CH\cdot CO_2H$, A., i, 335.
acylsemicarbazides and acylsemicarbazic acids, A., i, 417.
method of separation of stereoisomeric α-halogenated ethylenic acids (stable and labile), A., i, 647.
semicarbazones of α-ketonic acids; acylsemicarbazides and acylsemicarbazic acids, A., i, 688.
preparation of acylhydroxylamides from the [oximes] of α-ketonic acids, A., i, 694.
the estimation of antipyrine, A., ii, 344.
the action of iodine on the alkalis, A., ii, 368.
a new method for the estimation of aldoses, A., ii, 395.

Bourquelot, *Émile* [*Élie*], the biochemical synthesis of alkyl glucosides. IV. Alkyl galactosides, A., i, 379.
influence of glycerol on the activity of invertase, A., i, 731.

Bourquelot, *Émile*, and *A.* **Aubry**, influence of acetic acid on the synthesising and hydrolysing properties of β-glucosidase, A., i, 99.
crystallisation and complementary properties of the galactobiose previously obtained by biochemical synthesis, A., i, 250.
biochemical synthesis, by means of emulsin, of a second galactobiose, A., i, 250.

Bourquelot, *Émile*, *Marc* **Bridel**, and *A.* **Aubry**, crystallisation and properties of a β-monoglucoside of glycerol previously obtained by biochemical synthesis, A., i, 379.

Boutwell, *P. W.*, the phytic acid of the wheat kernel and some of its salts, A., i, 374.

Bouvet, *M.*, metallic salts of acetylsalicylic [*o*-acetoxybenzoic] acid, A., i, 650.

Bouyoucos, *George J.*, measurement of the inactive, or unfree, moisture in the soil by means of the dilatometer method, A., i, 510.

Bovard, *W. M.*, and *George Augustus* **Hulett**, inclusions in silver voltameter deposits and the electrochemical equivalent of silver, A., ii, 354.

Bowditch, *H. I.* See *Alfred W.* **Bosworth.**

Bowen, *Norman L.*, the sodium potassium nephelites, A., ii, 178.

Boyer. See **Bauzil.**

Bradford, *Samuel Clement*, adsorptive stratification in gels. II., A., ii, 366.

Bradley, *Harold Cornelius*, and *Joseph* **Taylor,** autolysis. V. Influence of bile on autolysis, A., i, 364.

Bräuer, *P.*, the second group in qualitative analysis, A., ii, 509.

Braham, *J. M.* See *Duncan A.* **MacInnes.**

Brahm, *C.*, the resorption and change of abnormally large amounts of sucrose and invert-sugar, A., i, 428.

Braley, *S. A.* See *George McPhail* **Smith.**

Branch, *Gerald Eyre Kirkwood*, the hydrolysis of hexahydropyrimidine, A., ii, 24.

Brander, *M.*, a series of four primary amines, having the amino-group linked to a tertiary carbon atom, and some of their derivatives, A., i, 555.
  the action of alcoholic ammonia on some alkylurethanes [carbamates], A., i, 560.

Brandt, *R.*, apparatus for estimating the noble gases [argon, etc.] and ~~nitrogen~~ by a gas-analysis method, A., ii, 384.

Brandt, *Rich.* See *Adolf* **Sieverts.**

Brannigan, *Peter Joseph*, and *Alexander Killen* **Macbeth,** the quantitative absorption of light by simple inorganic substances. I. The haloids of the alkali metals and hydrogen, A., ii, 2.

Braudo, (*Mlle.*) *Ek. Maks.* See *Michael A.* **Rakuzin.**

Braun, *Julius von*, rupture of the ring [nitrogen] in hydrohydrastinine and hydrocotarnine by means of cyanogen bromide, A., i, 162.
  the relative stability of the rings in cyclic bases under the conditions of the Hofmann reaction, A., i, 169.
  partial hydrolysis of biscyanamides, A., i, 173.
  tert.-aminobenzyl alcohols and their derivatives. V. Basic derivatives of benzophenone, A., i, 174.
  behaviour of sugars towards diphenylmethanedimethyldihydrazine, A., i, 251.
  o-vinylbenzyl bromide and its derivatives, A., i, 259.

Braun, *Julius von*, and *Z.* **Arkuszewski,** ethylene dibromide and dimethylaniline, A., i, 175.

Braun, *Julius von*, and *E.* **Aust,** the morphine alkaloids. V., A., i, 280.

Braun, *Julius von*, and *E.* **Danziger,** phenol bases. III., A., i, 263.

Braun, *Julius von*, *E.* **Danziger,** and *Z.* **Koehler,** the indene series. IV., A., i, 260.

Braun, *Julius von*, and *K.* **Heider,** *tert.*-aminobenzyl alcohols and their derivatives. VI. Trioxymethylene and dimethyl-*o*-toluidine, A., i, 175.

Braun, *Julius von*, *K.* **Heider,** and *L.* **Neumann,** scission of the hydrogenated indole and quinoline rings by reduction. III. Substituted hydroindole bases, A., i, 167.

Braun, *Julius von*, and *K.* **Kindler,** the morphine alkaloids. IV., A., i, 163.

Braun, *Julius von*, *Otto* **Kruber,** and *E.* **Danziger,** the indene series. III. 2-Amino-2-methylhydrindene from *o*-xylylene dicyanide, A., i, 130.

Braun, *Julius von*, and *E.* **Müller,** allylbetaine and allylhomocholine, A., i, 254.

Braun, *Julius von*, and *L.* **Neumann,** rupture of the hydrogenated indole and quinoline rings by reduction. IV. Methyltetrahydroquinoline, A., i, 282.

Braun, *R.* See *M.* **Fünfstück.**

Brauner, *Bohuslav*, the preparation of fluorine from tripotassium hydrogen plumbofluoride by chemical means, A., ii, 202.

Brauns, *Reinhard Anton*, scapolite-bearing bombs from the Laacher See district; refractive indices of sulphate-scapolite, A., ii, 325.

Bray, *William Crowell*, and *C. T.* **Dowell,** reactions between chlorine and ammonia, A., ii, 307.

Bray, *William Crowell.* See also *C. T.* **Dowell.**

Breazeale, *J. F.*, formation of "black alkali" (sodium carbonate) in calcareous soils, A., i, 724.

Breazeale, *J. F.* See also *Lyman James* **Briggs.**

Bredt, *Julius*, camphoceanaldehydic acid (*tert.-sec.*) (camphoric acid semialdehyde), A., i, 560.

Bredt, *Julius*, and *Wilhelm* **Holz,** β-*pericyclo*camphanone [Angeli's camphenone, Schiff's dehydrocamphor], A., i, 655.

Breukeleveen, *M. van*, microchemical estimation of small quantities of platinum in the presence of gold and silver, A., ii, 155.

Brewer, *G.* See (*Mrs.*) *Norah* **Radford.**

Brewster, *Joseph F.* See *Carl Oscar* **Johns.**

Breymesser, *Hermann.* See *Robert* **Kremann.**

Brezina, *Hans,* distillation of nicotine with steam, A., ii, 348.

Bridel, *Marc.* See *Émile* **Bourquelot.**

Briggs, *Lyman James,* and *J. F.* **Breazeale,** availability of potash in certain orthoclase-bearing soils affected by lime or gypsum, A., i, 511.

Briggs, *Samuel Henry Clifford,* the structure of inorganic compounds, T., 253; A., ii, 254.

Briggs, *T. Roland,* electrical endosmose. I., A., ii, 236.

Brigham, *Reed O.,* assimilation of organic nitrogen by *Zea mais* and the influence of *Bacillus subtilis* on such assimilation, A., i, 374.

Brightman, *Rainald,* action of nitric acid on castor oil, A., i, 626.

Brightman, *Rainald.* See also *Raphael* **Meldola.**

Brighton, *Thomas B.* See *Gilbert Newton* **Lewis.**

Brill, *Harvey C.,* seeds of *Pangium edule* and of *Hydnocarpus alcalæ,* A., i, 719.

Brinsmade, *James B.,* and *Edwin C.* **Kemble,** the occurrence of harmonics in the infra-red absorption spectra of diatomic gases, A., ii, 402.

Brinton, *Paul H. M. P.,* vanadates of glucinum, A., ii, 32.

Brislee, *Francis Joseph,* the changes in physical properties of aluminium with mechanical work. II. Specific heats of hard and soft aluminium, A., ii, 475.

Broderson, *H. G.* See *J. F.* **Lemp.**

Broek, *A. van den,* a general twin series of varieties of atoms, A., ii, 85.

Broeksmit, *T. C. N.,* citric acid and tartaric acid, A., ii, 429.

Brooks, *Benjamin T.,* and *Irwin W.* **Humphrey,** preparation of ethylene glycol, A., i, 533.

Brooks, *S. C.,* exosmosis, A., i, 371.
  a study of permeability by the method of tissue tension, A., i, 371.

Brown, *Adrian John,* and *Frank* **Tinker,** selective permeability; the absorption of phenol and other solutions by the seeds of *Hordeum vulgare,* A., i, 74.

Brown, *Bessie M.,* and *Solomon Farley* **Acree,** the reaction of both the ions and the non-ionised forms of acids, bases, and salts: the reaction of methyl iodide with sodium, potassium, and lithium ethoxides at 0°, A., ii, 24.

Brown, *F. E.* See *William Draper* **Harkins.**

Brown, *Glenn V.,* composition of thaumasite from Great Notch, New Jersey, A., ii, 146.

Brown, *Glenn V.* See also *Edgar Theodore* **Wherry.**

Brown, (*Miss*) *Janet Forrest McGillivray,* and *Robert* **Robinson,** veratric sulphinide, T., 952; A., i, 698.

Brown, *Maurice A.* See *Edward Sydney* **Simpson.**

Brown, *Mortimer J.,* silver peroxynitrate, A., ii, 88.

Brown, *Percy Edgar,* and *G. E.* **Corson,** ferrification in soils, A., i, 248.

Brown, *Percy Edgar,* and *E. B.* **Hitchcock,** the effects of alkali salts on nitrification, A., i, 717.

Brown, *William,* technique of preparing membranes for dialysis, A., ii, 362.

Brown, *W. G.* See *Ralph Gibbs van* **Name.**

Browne, *Vere Rochelle.* See *Frederick Palliser* **Worley.**

Browning, *Carl Hamilton, R.* **Gulbransen,** *Ernest Laurence* **Kennaway,** and *L. H. D.* **Thornton,** flavine and brilliant-green; powerful antiseptics with low toxicity to the tissues, A., i, 240.

Browning, *Kendall Colin,* detection of traces of mercury salts for toxicological purposes, T., 236; A., ii, 272.

Browning, *Philip Embury,* and *Lyman E.* **Porter,** separation and detection of gallium, A., ii, 544.

Browning, *Philip Embury,* and *Sewell E.* **Scott,** detection of germanium and its separation from arsenic, A., ii, 546.

Browning, *Philip Embury.* See also *Horace S.* **Uhler.**

Bruce, *E. L.,* magnesian tourmaline from Renfrew, Ontario, A., ii, 378.

Bruckmiller, *F. W.,* titration of magnesium, A., ii, 271.

Bruhns, *Gustav,* hydrogen oxalates of the alkali earth metals, A., i, 534.
  estimation of dissolved oxygen by Winkler's method, A., ii, 100.
  potassium dichromate as a standard. III., A., ii, 266.
  [titration of] alkalis and ammonia by oxalic acid and methyl-orange, A., ii, 270.
  potassium hydrogen carbonate as an analytical standard, A., ii, 419.

Brun, *Albert,* the volcanic exhalation, A., ii, 497.

Brunel, *Roger Frederick,* dissociation and rearrangement of *iso-* and *tert.*-butyl bromides in the gaseous state at high temperatures, and their formation from hydrogen bromide and *iso*butene, A., i, 625.

Brunel, *Roger Frederick.* See also *Marguerite* **Willcox.**

Bruni, *Giuseppe*, and *G.* **Levi**, ammoniates of silver salts. III., A., ii, 470.

Brunnschweiler, *Paul*. See *Adolf* **Kaufmann**.

Bruyn, *Cornelis Adriaan Lobry de*. See *Andreas* **Smits**.

Buchanan, *G. H.*, the occurrence of germanium in Missouri and Wisconsin blendes, A., ii, 416.

Bucher, *Armin*, the constitution of the tin–cadmium and tin–bismuth alloys, A., ii, 211.

Buchner, *Eduard*, and *Siegfried* **Skraup**, the extraction of different preparations of dried yeast, A., i, 613.
  the action of toluene on fermentation processes, A., i, 613.

Buckley, *J. B.*, *jun*. See *E. B.* **Holland**.

Buckmaster, *George Alfred*, capacity of blood and hæmoglobin to unite with carbon dioxide, A., i, 671.

Buckner, *G. Davis*. See *Joseph Hoeing* **Kastle**.

Büchner, *Ernst Hendrik*, and *Ada* **Prins**, vapour-pressures in the system: carbon disulphide–methyl alcohol, A., ii, 441.

Bürger, *Max*, the chemistry of the fats of tubercle bacilli, A., i, 499.

Bugge, *Günther*. See *Wilhelm* **Biltz**.

Buisson, *J. P. du*, the extraction and saturation of soils with volatile antiseptics, A., i, 529.

Bunzel, *Herbert Horace*, relationship existing between the oxydase activity of plant juices and their hydrogen-ion concentrations; the cause of oxydase activity in plant tissues, A., i, 107.

Burckhardt, *E.* See *Hans* **Rupe**.

Burdick, *Ch. L.* See *Richard* **Willstätter**.

Burgess, *P. S.* See *Charles Bernard* **Lipman**.

Burmann, *James*, rapid and accurate method of estimating dextrose, A., ii, 514.

Burnham, *W. S.* See *Charles W.* **Bennett**.

Burns, *Robert M.* See *Harry A.* **Curtis**.

Burns, *W. E.* See *C. Ferdinand* **Nelson**.

Burr, *K.* See *Hugo* **Kauffmann**.

Bury, *A.*, volumetric analysis of hypochlorite solutions used for sterilising water; rapid analysis of hydrogen peroxide, A., ii, 216.

Busch, *Max*, *Friedr.* **Achterfeldt**, and *Rud.* **Seufert**, isomeric hydrazones of glyoxylic acid, A., i, 228.

Busch, *Max*, and *Herm.* **Kunder**, autoxidation of benzaldehydephenylhydrazone in alcohol, A., i, 56.

Busvold, *N.*, synthesis of a basic calcium salt, on the ground of a change of properties of milk of lime, A., ii, 207.
  rapid method for the estimation of magnesium, A., ii, 218.

Butler, *B. S.*, and *Hoyt S.* **Gale**, alunite from Marysvale, Utah, A., ii, 490.

Bykov, *S. F.* See *P. N.* **Laschtschenko**.

Byl, *A. J.* See *Jacob* **Olie**, *jun*.

C.

Cabrera, *B.*, and *M.* **Marquina**, magnetochemistry of the compounds of chromium. I. Chromic sulphate and nitrate, A., ii, 355.

Cadre, *Shunker Trimbak*, and *John Joseph* **Sudborough**, additive compounds of *s*-trinitrobenzene with amino-derivatives of complex aromatic hydrocarbons, A., ii, 85.

Cahen, *Edward*, and *William Holdsworth* **Hurtley**, oxidation of the alkali butyrates by hydrogen peroxide with the production of succinic acid, A., i, 535.

Caldwell, *R. E.* See *R. H.* **Carr**.

Cammidge, *P. J.*, improved method of estimating sugar in the urine and blood, A., ii, 276.

Campbell, *Edward deMille*, formation of tricalcium aluminate, A., ii. 572.

Campbell, *W. R.* See *Andrew* **Hunter**.

Capps, *J. H.*, and *George Augustus* **Hulett**, coal distillation under pressure, A., i, 689.

Cardot, *Henry*. See *Charles* **Richet**.

Carles, *P.*, insoluble morphine in crude opium, A., i, 163.
  characterisation of urotropine, A., ii, 159.
  influence of calcium tartrate on the estimation of total tartaric acid (in crude tartars), A., ii, 278.

Carnot, *Adolphe*, ammonio-cobalt molybdate, tungstate, and vanadate; estimation and separation of cobalt, A., ii, 391.

Carr, *R. H.*, *George* **Spitzer**, *R. E.* **Caldwell**, and *O. H.* **Anderson**, efficiency of certain milk substitutes in calf feeding, A., i, 192.

Carruth, *Frank E.*, methods for approximating the relative toxicity of cottonseed products, A., i, 719.

Casale, *Luigi*, rotatory powers of tartrates of substituted amines, A., i, 378.

Casale, *Luigi,* amides and imides of tartaric acid, A., i, 545, 643.

Cashmore, *J. A.,* estimation of manganese in steel, A., ii, 43.

Cassel, *Henry W.,* decomposition of chloro- and bromo-acetic acid in alcoholic solution, A., ii, 249.

Catalán Sañudo, *Miguel,* new lines in the spectrum of magnesium, A., ii, 161.

Cath, *P. G.* See *Heike Kamerlingh* **Onnes.**

Cathrein, *Alois,* micro-diagnosis of a jadeite chisel, A., ii, 336.

Caton, *Frederick William,* obituary notice of, T., 312.

Cavazzi, *Alfredo,* a considerable error regarding the solubility of calcium carbonate in boiling water, A., ii, 532.
  estimation of phosphorus in cast iron, A., ii, 540.

Centnerszwer, *Mieczyslaw,* velocity of solution of metals. II. Velocity of solution of zinc in acids, A., ii, 135.

Cesaris, *Pietro de.* See *Nicola* **Parravano.**

Challinor, *Richard W.,* and *A. R.* **Penfold,** chemical examination of the oil from the Australian dugong, A., i, 239.

Chamot, *Emile Monnin,* and *Harriet Isabelle* **Cole,** use of textile fibres in microscopic qualitative chemical analysis, A., ii, 576.

Chamot, *Emile Monnin,* and *C. M.* **Sherwood,** culture media employed in the bacteriological examination of water. IV. Neutral-red lactose peptone media, A., ii, 556.

Chapman, *Alfred Chaston,* spinacene; a new hydrocarbon from certain fish liver oils, T., 56; A., i, 193.
  some main lines of advance in the domain of modern analytical chemistry, T., 203; A., ii, 266.
  colouring matter of red *Torulæ,* A., i, 244.

Chapman, *S.,* the partial separation by thermal diffusion of gases of equal molecular weight, A., ii, 444.

Charpy, *Georges,* and *S.* **Bonnerot,** the heterogeneity of steels, A., ii, 573.

Charpy, *Georges,* and *Marcel* **Godchot,** the oxidation of coal, A., ii, 103.

Chase, *Wallace S.,* decomposition of cerous oxalate in a reducing or inert atmosphere and a new property of the higher oxides of cerium, A., ii, 475.

Chaskelis, *P.* See *Siegmund* **Reich.**

Chattaway, *Frederick Daniel,* the crystallisation of calcium tartrate, A., i, 4.

Chatterjee, *Nihar Ranjan.* See *Rasik Lal* **Datta.**

Chauvenet, *Édouard,* the zirconyl radicle (ZrO), A., ii, 264.
  the zirconyl bromides, A., ii, 321.
  zirconium fluorides and zirconyl fluorides, A., ii, 322.
  the compounds of zirconium oxide with sulphuric acid, A., ii, 322.
  the zirconyl sulphates, A., ii, 374.
  zirconyl acid sulphate, A., ii, 416.

Chemische Fabrik auf Aktien (vorm. *E.* Schering), 2-naphthylquinoline-4-carboxylic acids, A., i, 96.

Chemische Fabrik Griesheim Elektron, preparation of transformation products of ω-dibromo-2-*p*-toluoylbenzoic acid, for example, anthraquinone-2-aldehyde, A., i, 40.
  manufacture of anthracene dyestuffs [alkylated pyrazoleanthrone yellow], A., i, 56.
  preparation of acyl derivatives of 6-amino-α-naphthol-3-sulphonic acid, A., i, 453.
  preparation of chloro-derivatives of *N*-dihydro-1:2:1′:2′-anthraquinoneazine [indanthrene], A., i, 479.

Chernoff, *Lewis H., Arno* **Viehoever,** and *Carl Oscar* **Johns,** saponin from *Yucca filamentosa,* A., i, 191.

Chevenard, *P.,* anomaly of cementite in carbon steels, annealed, tempered, and half-tempered, A., ii, 372.
  mechanism of the tempering of carbon steels, A., ii, 414.

Chick, *O.* See *Bernard Farmborough* **Howard.**

Chikashige, *Masumi,* and *Isaburo* **Saito,** metallographic study of the system silver–tellurium, A., ii, 139.

Chikashige, *Masumi,* and *Yoshimoto* **Yamauchi,** metallographic study of the system antimony sulphide–cuprous sulphide, A., ii, 113.

Chiò, *Mario,* carbon dioxide and the coagulation of blood, A., i, 672.

Choudhury, *Jogendra Kumar.* See *Rasik Lal* **Datta.**

Chowdhuri, *Tarini Charan,* inquiries into the explanation of radium disintegration, A., ii, 402.

Chowdhuri, *Tarini Charan.* See also *Panchānan* **Neogi.**

Christensen, *Anders C.,* thalleioquinine, A., i, 51.
  the action of ammonium monosulphide on mercuric sulphide, A., ii, 33.

Christensen, *C.* See *O. B.* **Böggild.**

Christensen, *Harald R.,* methods for determining the reaction of soils, A., i, 684.

Christiansen, *E.* See *Valdemar* **Henriques.**

Christiansen, (*Miss*) *Johanne*, hydrates of alcohols and fatty acids. II., A., ii, 404.

Christiansen, *J. A.*, dissociation of salicylic acid, A., ii, 25.

Christiansen, *J. A.* See also *Svend* **Lomholt.**

Christie, *A. W.* See *George P.* **Gray.**

Chrzaszcz, *Tadeusz*, and *A.* **Joscht,** the inhibition of the single amyloclastic functions of amylase of malt produced by keeping in the presence of various reagents, A., i, 423.

Chuchrikova, (*Mlle.*) *A. M.* See *S. S.* **Nametkin.**

Chur, *M.* See *Otto* **Fischer.**

Chwolson, *O. D.*, the atomic weights, A., ii, 27.

Ciamician, *Giacomo Luigi*, and *Ciro* **Ravenna,** influence of certain organic substances on the development of plants. I., A., i, 244.
  behaviour of some organic substances in plants. VIII., A., i, 681.

Claasz, *Max*, constitution of the blue isatin salts, A., i, 413.

Clack, *Basil W.*, diffusion in liquids, A., ii, 75.

Clarens, *J.*, methods of titrating mixtures of hydrogen carbonate and carbonate or of alkali carbonate and hydroxide necessitating neither weighing nor previously titrated solutions, A., ii, 507.

Clark, *A. L.* See *Johan Pieter* **Kuenen.**

Clark, *E. P.*, preparation of lyxose, A., i, 632.

Clark, *Friend Ebenezer*, *S. F.* **Cox,** and *E.* **Mack,** chloroethers. I. The action of chlorodimethyl ether on salts of organic acids, A., i, 316.

Clark, *George L.* See *William Draper* **Harkins.**

Clark, *William Mansfield*, and *Herbert A.* **Lubs,** improved chemical methods for differentiating bacteria of the coli-aerogenes family, A., i, 528.
  a substitute for litmus for use in milk cultures, A., ii, 499.

Clarke, *Frank Wigglesworth*, the constitution of melilite and gehlenite, A., ii, 417.

Clausmann, *Paul.* See *Armand* **Gautier.**

Clemente, *Amando.* See *George W.* **Heise.**

Clementi, *Antonio*, formation of urea by arginase and the specificity of its action, A., i, 358.
  factors necessary for the formation of carbamide from ammonia and carbon dioxide in the isolated liver. I. Behaviour of ammonium carbonate circulated with Ringer's solution through the isolated liver, A., i, 674.
  the possibility of titrating mono-substituted amino-groups of amino-acids and formaldehyde, A., ii, 344.
  micro-titration with formaldehyde and its applications in physiology. III. Detection of arginase, A., ii, 400.

Clennell, *J. E.*, analysis of aluminium dust, A., ii, 335.

Close, *Harold Wilberforce.* See *Hugh Stott* **Taylor.**

Clowes, *George Henry Alexander*, antagonistic electrolytes and jelly formation, A., ii, 245.

Coehn, *Alfred*, and *Karl* **Stuckardt,** action of light on the formation and decomposition of the hydrogen halogen acids, A., ii, 5.

Cohen, *Ernst*, and *A. M.* **Valeton,** piezo-chemical studies. XIV. Influence of pressure on the velocity of reaction in condensed systems. III., A., ii, 566.

Colani, *A.*, solubility of alkali oxalates in the presence of some alkali salts, A., i, 78.
  the system water–uranyl oxalate–sodium oxalate, A., i, 513.
  the system water–uranyl oxalate–ammonium oxalate, A., i, 535.
  action of metaphosphoric acid on the oxides of molybdenum, A., ii, 479.

Cole, *Harriet Isabelle.* See *Emile Monnin* **Chamot.**

Coleman, *Warren.* See *John Raymond* **Murlin.**

Colin, *H.*, the antiseptic properties of nitrous air, A., ii, 466.

Collings, *C. H.*, apparatus for the recovery of bromine, A., ii, 29.

Colomba, *Luigi*, cyanotrichite and dioptase from Traversella, A., ii, 377.

Colson, *Émile*, the constitution of cyanamide, T., 554; A., i, 448.

Colver, *Edward de Wykersley Swyft*, and *Edmund Brydges Rudhall* **Prideaux,** stannous chloride reduction method for estimating nitrotoluenes, A., ii, 340.
  estimation of nitrotoluenes, A., ii, 512.

Coma y Roca, *F.*, transformation of α-glycols, A., i, 266.

Compagnie des Produits Chimiques d'Alais et de la Camargue, preparation of benzenesulphonic acid, A., i, 515.

Conant, *James Bryant,* preparation of benzyl chloride, A., i, 640.

Conant, *James Bryant.* See also *Elmer Peter* **Kohler.**

Conev, *N. S.*, reaction of ethereal complexes of metal haloids with aromatic hydrocarbons, A., i, 135.

Conner, *M. F.* See *Charles H.* **Warren.**

Conno, *E. de'*, action of aromatic amines on aliphatic acids, A., i, 386.

Contardi, *Angelo.* See *Wilhelm* **Körner.**

Cook, *Frank C.*, and *J. B.* **Wilson,** effect of three annual applications of boron on wheat, A., i, 721.

Cook, *R. C.*, and *F. E.* **Allison,** the effect of soil reaction on the availability of ammonium sulphate, A., i, 623.

Cook, *R. C.* See also *F. E.* **Allison.**

Cooke, *Raymond D.* See *Paul* **Rudnick.**

Cooper, *Christopher.* See *Aquila* **Forster.**

Cooper, *Lenna.* See *Mary S.* **Rose.**

Cope, *W. C.*, and *Jacob* **Barab,** application of the nitrometer for the determination of constitution and estimation of nitrogen in a class of nitro-compounds (nitroamines), A., ii, 40.

"nitron" as a gravimetric reagent for the analysis of substances used in explosives, A., ii, 268.

Copisarow, *Maurice,* the Friedel-Crafts' reaction. I. Phthalyl chloride and the mechanism of its reaction with benzene, T., 10; A., i, 144.

Coquet, *C. de*, estimation of ferricyanides by titration with permanganate, A., ii, 551.

Cornish, (*Miss*) *Elfrida Constance Victoria,* and *Robert Stenhouse* **Williams,** colour changes produced by two groups of bacteria on caseinogen and certain amino-acids, A., i, 613.

Corson, *G. E.* See *Percy Edgar* **Brown.**

Corti, *A.*, separation of glutamic acid from other amino-acids, A., i, 634.

Coste, *John Henry,* the absorption of atmospheric gases by water, A., ii, 463.

Covitz, *P.*, estimation of nickel in iron ores, A., ii, 153.

Cox, *S. F.* See *Friend Ebenezer* **Clark.**

Craig, *Thomas J. I.*, volumetric estimation of sulphur in pyrites, A., ii, 420.

Crann, *Thomas William.* See *Harry Medforth* **Dawson.**

Craver, *L. F.* See *John Raymond* **Murlin.**

Crawford, *C. W.* See *C. K.* **Francis.**

Crede, *Eduard.* See *Robert B.* **Krauss.**

Cremer, *Max,* and *Rudolf* W. **Seuffert,** [with **Berger, Pape,** and **Fabischel**], sugar formation. I. Experiments with glycine, glycine anhydride, amino-ethyl alcohol and glycolaldehyde, A., i, 240.

Crinis, *Max de*, new method for the estimation of the total volume of blood in man, A., i, 489.

Crombie, *John N.* See *Marks* **Neidle.**

Crommelin, *Claude Auguste.* See *Heike Kamerlingh* **Onnes.**

Crossley, *M. L.*, a hydrate of sodium anthraquinone-2:7-disulphonate, A., i, 346.

Crossley, *M. L.*, and *C. B.* **Ogilvie,** the action of sulphuric acid on certain nitrocarbocyclic compounds. I. The action on nitrobenzene, A., i, 328.

Crowther, *Charles,* and *Alexander* **Hynd,** distribution of the fatty acids in the milk fat of the cow and sheep, A., i, 608.

Cullen, *Glenn E.*, acidosis. III. Electrometric titration of plasma as a measure of its alkaline reserve, A., i, 521.

Cullen, *Glenn E.* See also *Donald D. van* **Slyke,** and *Edgar* **Stillman.**

Cunningham, (*Miss*) *Mary,* and *Charles* **Dorée,** the chemistry of caramel, T., 589; A., i, 513.

Currie, *James N.*, citric acid fermentation of *Aspergillus niger*, A., i, 614.

Curtis, *Harry A.*, and *Robert M.* **Burns,** non-aqueous solutions. I. Reactions in *iso*amyl alcohol solutions, A., ii, 260.

Curtius, *Theodor,* and *Hartwig* **Franzen,** some chemical constituents of green plants. VIII. Detection of formaldehyde in plants. IX. Some non-volatile, water-soluble constituents of the leaves of the edible chestnut, A., i, 438.

Curtius, *Theodor,* [with *Bernhard van der* **Laan,** *David* **Aufhäuser,** *Alfred* **Goldberg,** *Carl von* **Hofe,** *Christian* **Ohlgart,** *August* **Darapsky,** and *Friedrich* **Sauvin**], the special reactions in the transformation of the azides of the carboxylic acids. VII. XIII., A., i, 635.

Curtius, *Theodor,* [with *Adrien* **Laurent,** *William F.* **Zimmerli,** and *Georg* **Petridis**], mixed chains containing carbamide, methylenediamine, and amino-acid residues, A., i, 199.

Curtman, *Louis J.*, and *M.* **Freed,** modified Benedict and Hitchcock uric acid standard solution, A., ii, 107.

Curtman, *Louis J.*, and *Ben R.* **Harris,** systematic detection of thiocyanates, A., ii, 108.

Curtman, *Louis J.*, and *Ben R.* **Harris,** the interference of thiocyanates, ferrocyanides, and ferricyanides in the detection of iodides with palladium, A., ii, 267.
the inadequacy of the basic ferric acetate test for acetates, A., ii, 516.

Cusmano, *Guido*, reduction of nitro- and nitroso-compounds with platinum and hydrogen, A., i, 641.

Cusmano, *Guido.* See also *Angelo* **Angeli.**

Cykina, *O.* See *E.* **Grischkevitsch-Trochimovski.**

Czaporowski, *L.* See *St.* **Opolski.**

Czochralski, *J.*, a new method for the measurement of the velocity of crystallisation of the metals, A., ii, 302.

D.

Dafert, *Franz Wilhelm*, and *Alfred* **Uhl,** phospham, A., ii, 203.

Dakin, *Henry Drysdale*, oxidation of amino-acids and of related substances with chloramine-T., A., i, 542.

Dakin, *Henry Drysdale*, and *E. K.* **Dunham,** disinfection of drinking-water: with a description of a new substance for the preparation of stable tablets for the sterilisation of polluted water, A., i, 433.

Dale, *J. K.*, preparation of bromoacetylglucose and certain other bromoacetyl sugars, A., i, 7.

Dale, *J. K.* See also *Claude S.* **Hudson.**

Dam, *C. van*, a new olfactometer, A., i, 606.
adsorption of odoriferous substances, A., i, 607.

Damm, *Paul.* See *Heinrich* **Biltz.**

D'Ans, *Johannes*, [with *A.* **Bertsch** and *A.* **Gessner**], oceanic salt deposits, A., ii, 176.

Danysz, *Jean*, the physico-chemical properties of the products of the group of the arsenobenzenes; their transformation in the organisms, A., i, 430.
metallic derivatives of diaminodihydroxyarsenobenzene, A., i, 599.

Danziger, *E.* See *Julius von* **Braun.**

Darapsky, *August.* See *Theodor* **Curtius.**

Datta, *Rasik Lal*, and *Nihar Ranjan* **Chatterjee,** halogenation. XIV. Bromination of hydrocarbons by means of bromine and nitric acid, A., i, 15.
halogenation. XV. Direct iodination of hydrocarbons by means of iodine and nitric acid, A., i, 327.

Datta, *Rasik Lal*, and *Jogendra Kumar* **Choudhury,** halogenation. XIII. Methods of estimation of semicarbazide, semioxamazide, and oxalylhydrazide by their interactions with halogens and halogen oxy-acids, A., ii, 108.

Datta, *Rasik Lal*, and *Nogendra* **Prosad,** halogenation. XVI. Iodination by means of nitrogen iodide or by means of iodine in the presence of ammonia, A., i, 332.

Datta, *Rasik Lal*, and *Jnanendra Nath* **Sen,** indirect formation of double salts. VI. The double silver, lead, bismuth, copper, and mercurous haloids of substituted ammonium bases, A., i, 323.
normal potassium persulphate as a reagent in organic chemistry, A., i, 329.

Daughters, *Milo Reason*, action of sodium benzyl cyanide on ethyl *p*-tolylcinnamate, A., i, 647.

Dauvillier, *A.* See *R.* **Ledoux-Lebard.**

David, estimation of ozone, A., ii, 216.

Davidsohn, *J.*, estimation of unsaponifiable matter in oils and fats, A., ii, 183.

Davies, *Edward*, obituary notice of, T., 323.

Davies, *Earl C. H.* See *William Draper* **Harkins.**

Davis, *Charles W.*, the phenoldisulphonic acid method for estimating nitrates in soils, A., ii, 329.

Davis, *Charles W.* See also *G. A.* **Perley.**

Davis, *Harold S.*, the rhythmic precipitation of colloidal mercury, A., ii, 452.

Davis, *Harold S.* See also *Theodore William* **Richards.**

Davis, *J. H.* See *John James Rickard* **Macleod.**

Davison, *A. W.*, adsorption of chromium oxide by hide powder, A., ii, 241.

Dawson, *Harry Medforth*, and *Thomas William* **Crann,** the dual theory of acid catalysis; a comparison of the activities of certain strong acids, A., ii, 26.

Day, *F. W. F.* See *B. J.* **Eaton.**

De, *Rajendra Lal*, relationship between the physical properties of isomeric cobaltammines and the electro-valencies of their co-ordination complexes, T., 51; A., ii, 165.

Débourdeaux, *Léon*, estimation of theobromine, A., ii, 348.

Debus, *Heinrich*, obituary notice of, T., 325.

Debye, *Peter*, the first electron ring of the atoms, A., ii, 434.
the arrangement of the atoms in tungsten, A, ii, 574.
Debye, *Peter*, and *P.* **Scherrer**, interference effects of irregularly orientated particles in Röntgen light. III. The constitution of graphite and amorphous carbon, A., ii, 437.
Dedichen, *Herman*. See *O. M.* **Halse**.
Dehn, *William Maurice*, the mass action of water on dyes, A., i, 578.
colorimetric determination of the solubilities of helianthin and its salts, A., i, 594.
comparative solubilities in water, pyridine, and in aqueous pyridine, A., ii, 445.
fallacies in colorimetry, A., ii, 499.
Dehn, *William Maurice*, and *Alice A.* **Ball**, colorimetric studies of picrate solutions, A., i, 556.
Dehn, *William Maurice*, and *Lois* **McBride**, chromoisomerism of methyl-orange, A., i, 594.
Deichsel, *St.* See *Konrad* **Schaefer**.
Dejean, *P.*, the formation of troostite and martensite, A., ii, 477.
the classification of nickel steels and manganese steels, A., ii, 477.
martensite, troostite, sorbite, A., ii, 535.
Delépine, *Marcel*, complex salts; the preparation of potassium iridotrioxalate and the optical resolution of the iridotrioxalates, A., i, 627.
the chlorides and chloro-salts of iridium, A., ii, 537.
Delprat, *M.* See *Thorburn Brailsford* **Robertson**.
Deming, *Horace G.*, the nomon—a calculating device for chemists, A., ii, 567.
a universal gas-volumeter, A., ii, 576.
Demoussy, *Ém.* See *Leon* **Maquenne**.
Denham, *Henry George*, lead subiodide and an improved method for preparing lead suboxide; the solubility of lead iodide, T., 29, A., ii, 141.
Denham, *William Smith*, and (*Miss*) *Hilda* **Woodhouse**, trimethyl glucose [dextrose trimethyl ether] from cellulose, T., 244, A., i, 320.
Denigès, *Georges*, differentiation of the two naphthols by the titanic acid-sulphuric acid reagent, A., ii, 48.
sodium perchlorate as a general reagent in microchemistry, A., ii, 345.
microreactions of the perchloric ion, A., ii, 419.
Denis, *Willey*, cholesterol in human blood under pathological conditions, A., i, 236.
Denis, *Willey*, and *J. G.* **Kramer**, [with *Anna S.* **Minot**], influence of protein intake on creatine excretion in children, A., i, 526.
Denis, *Willey*, [with *Anna S.* **Minot**], diurnal variations in creatine excretion, A., i, 367.
influence of the protein intake on the excretion of creatine in man, A., i, 496.
production of creatinuria in normal adults, A., i, 676.
Dennis, *Louis Monroe*, method of separating benzenedisulphonic acid from sulphuric acid and converting it into a salt, A., i, 515.
Derick, *Clarence G.*, and *D. W.* **Bissell**, trimethylene [$\alpha\gamma$-propylene] oxide. I. Preparation and characterisation, A., i, 1.
Derick, *Clarence G.*, and *Oliver* **Kamm**, correlation of ionisation and structure in unsaturated acids, A., ii, 233.
Dernby, *Karl Gustav*, a comparative study of the proteolytic enzymes—erepsin from the intestine and ereptase from yeast, A., i, 234.
the proteolytic enzymes of *Pinguicula vulgaris*, A., i, 438.
the proteoclastic ferments of yeast and their relationship to autolysis, A., i, 500.
the proteoclastic enzymes of *Drosera rotundifolia*, A., i, 506.
the kinetics of an enzymatic hydrolysis of glycylglycine, A., ii, 82.
Descamps, *L.*, the analysis of gases by means of Orsat's apparatus, replacing pyrogallol by hyposulphites, A., ii, 216.
Deutsche Gold- & Silber-Scheideanstalt vorm. Roessler, preparation of sodium perborate, A., ii, 139.
preparation of alkali perborates, A., ii, 139.
Deventer, *Charles Marius van*, galvanic ennobling of metals, A., ii, 11.
Dey, *Manik Lal*. See *Prafulla Chandra* **Rây**.
Dezani, *Serafino*, formation of thiocyanic acid in animals, A., i, 676.
a very delicate reaction of the nitriles, A., ii, 549.
Dhar, *Nilratan*, catalysis. III. Some induced reactions, T., 690, A., ii, 458.
catalysis. IV. Temperature co-efficients of catalysed reactions, T., 707, A., ii, 458.
Dhéré, *Charles*, hæmocyanin, A., i, 236.
acid hæmochromogen, A., i, 519.

Dhéré, *Charles*, *L.* **Baudoux**, and *A.* **Schneider**, the crystallisation of acid hæmochromogen, A., i, 712.

Dhéré, *Charles*, and *G.* **Vegezzi**, helicorubin, A., i, 421.

Diels, *Otto*, carbon suboxide, A., ii, 370.

Dienert, *F.*, and *F.* **Wandenbulke**, estimation of free chlorine in hypochlorite solutions, A., ii, 419.

Diesselhorst, *H.*, and *Herbert* **Freundlich**, fibrin regarded as an anisotropic, amorphous, solid substance, A., i, 180.

Dilthey, *Walther*, pyrylium compounds. II. and III., A., i, 578, 660.

Dinwiddie, *Joseph G.*, separation of hydrofluoric acid and hydrofluosilicic acid, A., ii, 39.
  estimation of fluorine in soluble fluorides, A., ii, 99.

Disselkamp, *P.* See *Paul* **Pfeiffer.**

Dittler, *Emil*, minium from Biberwier, Tyrol, A., ii, 144.
  adsorption of sulphuric acid by ferric hydroxide and formation of colloidal sulphur from sulphides, A., ii, 443.
  further experiments on the synthesis of wulfenite, A., ii, 491.

Ditz, *Hugo*, and *Franz* **Kanhäuser**, the solubility of lead sulphate in highly concentrated and fuming sulphuric acid, A., ii, 208.

Dixon, *Augustus Edward*, salts of thiocarbamide, T., 684; A., i, 545.

Dixon, *Augustus Edward*, and *John* **Taylor**, the interaction of aldehydes and thiocarbamides in the presence of acids, A., i, 11.

Djenab, *Kemal*, and *Carl* **Neuberg**, saccharophosphatase of yeasts and the fermentation of sucrose phosphoric acid, A., i, 680.

Doelter [y Cisterich], *Cornelis* [*August*], natural and artificial ultramarine, A., ii, 147.
  composition of pyroxenes, A., ii, 378.
  equilibrium in silicate fusions and the determination of the melting-point of calcium silicate, A., ii, 456.

Doisy, *E. A.* See *Otto* **Folin.**

Dolch, *P.* See *Fritz* **Foerster.**

Dollwig, *H. C.*, *A. C.* **Kolls**, and *Arthur Solomon* **Loevenhart**, the effect of the partial pressure of oxygen on combustion, A., ii, 569.

Domanicki, *N.*, reaction of sulphur chloride with metals; catalytic action of ether, A., ii, 369.

Donau, *Julius.* See *Rudolf* **Scharizer.**

Dorée, *Charles.* See (*Miss*) *Mary* **Cunningham.**

Dorner, *K.* See *Kurt* **Hess.**

Doubt, *Sarah L.*, sensitiveness of plants to poisoning with coal gas, A., i, 619.

Dover, (*Miss*) *Mary Violet*, and *John W.* **Marden**, comparison of the efficiency of some common desiccants, A., ii, 500.

Dover, (*Miss*) *Mary Violet.* See also *John W.* **Marden.**

Dow Chemical Co., The, preparation of carbon tetrachloride, A., i, 77.

Dowell, *C. T.*, and *William Crowell* **Bray**, experiments with nitrogen trichloride, A., ii, 306.

Dowell, *C. T.* See also *William Crowell* **Bray.**

Downs, *C. R.* See *John Morris* **Weiss.**

Dox, *Arthur Wayland*, synthesis of a naphthatetrazine from ethyl succinylsuccinate and dicyanodiamide, A., i, 481.

Dox, *Arthur Wayland*, and *W. G.* **Gaessler**, an iodine additive product of coumarin, A., i, 346.

Dox, *Arthur Wayland*, and *A. R.* **Lamb**, an accurate aeration method for the estimation of alcohol in fermentation mixtures, A., ii, 47.

Dox, *Arthur Wayland*, and *G. P.* **Plaisance**, condensation of thiobarbituric acid with aromatic aldehydes, A., i, 53.
  the occurrence and significance of mannitol in silage, A., i, 683.
  estimation of vanillin in vanilla extract, A., ii, 53.
  a comparison of barbituric acid, thiobarbituric acid, and malonylguanidine as quantitative precipitants for furfuraldehyde, A., ii, 53.

Dox, *Arthur Wayland*, and *C. W.* **Roark**, *jun.*, the determination of the gelatinisation temperatures of starches by means of an electrically heated chamber on the microscope stage, A., ii, 276.

Drakeley, *Thomas James*, liberation of hydrogen sulphide from gob fires in coal mines, T., 853; A., ii, 530.

Dreyfus, *Henry*, preparation of acetic acid and acetaldehyde from acetylene, A., i, 2.
  preparation of anhydrides of aliphatic acids, A., i, 2.
  preparation of acetic anhydride, A., i, 194, 441.

Druce, *John Gerald Frederick*, a simple method of preparing potassium stannichloride, T., 418; A., ii, 309.

Drucker, *Carl*, fluidity. I., A., ii, 409.

Drummond, *Jack Cecil.* See *William Dobinson* **Halliburton.**

Drushel, *William Allen*, and *A. R.* **Felty**, the preparation and ionisation of the dialkyl hydrogen phosphates and benzenedisulphonic acids, A., i, 126.

Dubin, *Harry*, influence of inositol on the excretion of phenol in the dog, A., i, 187.
  influence of bile on the production of phenol, A., i, 602.

Dubreuil, *J.* See *L.* **Tribondeau.**

Ducháček, *Franz*, *Bacillus paralacticus*, A., i, 612.

Duin, *C. F. van*, trinitrophenylmethylnitroamine (tetranitromethylaniline), A., i, 554.
  action of organo-magnesium compounds on, and reduction of, cineol, A., i, 655.
  estimation of tungsten and silicon in tungsten steel, A., ii, 181.

Dumanski, *A. V.*, and (*Mlle.*) *A. V.* **Zvereva**, action of ammonia and calcium on benzene, A., i, 124.

Dumesnil, *Philippe*, synthesis by means of sodamide; preparation and study of new mono- and di-ketones, A., i, 653.

Dunham, *E. K.* See *Henry Drysdale* **Dakin.**

Dunnicliffe, *Horace Barratt*, a simple method for the purification of mercury, A., ii, 414.

Dunstan, *Albert Ernest.* See *Ernest Lawson* **Lomax.**

Dupuy, *Eugene Louis.* See *Henri* **Le Chatelier.**

Durrant, *Reginald Graham*, numerical relation of atomic weights to atomic numbers, A., ii, 253.

Duschak, *L. H.*, and *S. O.* **Spencer**, an improved mercury still, A., ii, 316.

Dutoit, *Paul*, and *Meyer* **Lévy**, estimation of the alkaloids by physico-chemical volumetric methods, A., ii, 225.

Dutt, *Barun Chandra*, and *Surya Narayan* **Sen**, the action of nitric oxide on metallic peroxides suspended in water, A., ii, 85.

Dyer, *D. C.*, estimation of the volatile fatty acids; colorimetric qualitative reactions for their identification, A., ii, 157.

E.

Eaton, *B. J.*, and *F. W. F.* **Day**, estimation of free and combined sulphur in vulcanised rubber, and the rate of combination of sulphur with different types of plantation Para rubber, A., ii, 150.

Eberhard, *August*, aminophenylethylcarbinol [β-amino-α-phenylpropyl alcohol], A., i, 392.
  zinc platinichloride, A., ii, 313.

Ebert, *Ralf.* See *Karl Andreas* **Hofmann.**

Eberwein, *St.* See *Josef* **Herzig.**

Eble, *Karl.* See *Wilhelm* **Wislicenus.**

Eckert, *Alfred*, the course of the reaction which takes place when higher unsaturated fatty acids are fused with potassium hydroxide, A., i, 317.

Eckert, *Alfred*, and *Rudolf* **Pollak**, reduction in concentrated sulphuric acid solution by means of aluminium powder, A., i, 345.

Eckler, *C. R.* See *A. L.* **Walters.**

Eckles, *C. H.*, and *Leroy S.* **Palmer**, influence of parturition on the composition and properties of the milk and milk fat of the cow, A., i, 68.

Eckweiler, *H. W.* See *Sara Stowell* **Graves.**

Edelmann, *Adolf*, a test for albumin for use by the military surgeon, A., ii, 110.

Eder, *Josef Maria*, arc spectra of yttrium, erbium, and their intermediate fractions, A., ii, 1.
  the arc spectrum of samarium, A., ii, 185.

Eder, *Robert*, detection of atropine and related mydriatic alkaloids, A., ii, 346.
  commercial chrysarobin. II., A., i, 464.

Edgar, *Graham*, reduction of vanadic acid by hydriodic acid, A., ii, 36.
  conductivity measurements on oxidation-reduction reactions, A., ii, 288.

Edlbacher, *Siegfried*, action and occurrence of arginase, A., i, 670.

Edwards, *J. D.*, determination of gas density, A., ii, 442.

Effront, *Jean*, achroodextrinase, A., i, 301.

Efremov, *S. V.* See *P. N.* **Laschtschenko.**

Eggert, *J.*, the Landolt reaction, A., ii, 197.

Eggert, *J.*, and *H.* **Schimank**, lecture experiments on the theory of explosives, A., ii, 462.

Egloff, *Gustav*, thermal and pressure decomposition of pentanes and hexanes, A., i, 109.
  analysis of light oils [for benzene, toluene, and xylene], A., ii, 338.

Egloff, *Gustav*, and *Robert J.* **Moore**, cracking of an aromatic base oil; the temperature factor at constant rate under pressure, A., i, 385.

Egloff, *Gustav*, and *Thomas J.* **Twomey**, effect of temperature on the formation of benzene, toluene, xylene, naphthalene, and anthracene from petroleum at atmospheric pressure, A., i, 110.

Egloff, *Gustav*. See also *Joaquin Enrique* **Zanetti**.

Egorkin, *N. I.* See *J. S.* **Zalkind**.

Ehrenberg, *Paul*, *Erna* **Hahn**, and *Otto* **Nolte**, formation of layers in suspensions of soils and clays; their explanation and their application in the investigation of soils for agricultural purposes, A., ii, 453.

Ehrenberg, *Paul*, and *Otto* **Nolte**, influence of manganese taken up by plants on their composition, A., i, 504.

Ehrlich, *Felix*, the detection of tyrosol and tryptophol in products of fermentation, A., i, 309.
  the vegetation of yeasts and moulds on heterocyclic nitrogen compounds and alkaloids, A., i, 309.
  pectin substances, their constitution and importance, A., i, 321.

Eichel, *A.* See *Kurt* **Hess**.

Eicke, detection of albumin in urine, A., ii, 110.

Eitel, *W.*, systems of many components, A., ii, 565.

Ekeley, *John Bernard*, and *Clifford* **Banta**, the salts of phthalic acid, A., i, 338.

Elbs, *Karl*, example of a reversible reaction and complex salt formation, A., ii, 371.

Elion, *H.*, a new bromine method for the estimation of thymol, salicylates, and similar compounds, A., ii, 514.

Ellinger, *Alexander*, and *Otto* **Riesser**, porphyrin occurring in urine after trional-poisoning, A., i, 715.

Ellis, *Carleton*, and *Louis* **Rabinovitz**, esters of oleic acid and their hydrogenated products, A., i, 78.

Elvert, *Heinrich*. See *Wilhelm* **Wislicenus**.

Elvove, *Elias*, detection and estimation of small amounts of methyl alcohol, A., ii, 341.
  colorimetric estimation of small amounts of aniline, A., ii, 584.

Embden, *Gustav*, and *Salo* **Isaac**, formation of lactic acid and acetoacetic acid in the livers of diabetic animals, A., i, 496.

Embden, *Gustav*, and *Fritz* **Laquer**, chemistry of lactacidogen. II., A., i, 674.

Emery, *William O.*, and *Samuel* **Palkin**, organic periodides. II. Periodides of antipyrine, iodoantipyrine, and pyramidone, A., i, 54.

Emich, *Friedrich*, microchemical detection of carbon and sulphur, A., ii, 218.

Emmert, *Bruno*, compounds of pyridine with the alkali metals. III., A., i, 221.

Endle, *R.* See *Hermann* **Staudinger**.

Engfeldt, *N. O.*, Shaffer's oxidation method for the estimation of β-hydroxybutyric acid in urine, A., ii, 398.
  estimation of the acetone substances in urine, together with an altered procedure for a separate estimation of acetone and acetoacetic acid in urine, A., ii, 550.

Engle, *Edgar W.*, and *Clarence William* **Balke**, rare earths, A., ii, 259.

Enklaar, *Cornelis Jacobus*, refractometric investigations of hydrocarbons with two and three conjugate double linkings at the same time; the aliphatic terpenes and their derivatives; synthesis of new αγε-trienes, A., i, 111.
  the melting-points of some hydrocarbons, in particular of dienes, having a system of conjugate double linkings, A., i, 113.
  the aliphatic terpenes, A., i, 377.
  sources of error in the analysis of volatile substances which are difficult to burn, and a method by which accurate results can be obtained, A., ii, 152.

Entat, *M.* See *E.* **Vulquin**.

Eoff, *John R.*, *jun.*, lævulose the preponderant sugar of apple juices, A., i, 531.

Ephraim, *Fritz*, the nature of subsidiary valencies. XV. Polyhaloids, A., ii, 531.

Ephraim, *Fritz*, and *Seb.* **Millmann**, the nature of subsidiary valencies. XIV. Influence of valency on the energy of subsidiary valencies, A., ii, 319.

Ephraim, *Fritz*, and *Paul* **Wagner**, the nature of subsidiary valencies. XVI. The intensity of the attachment of water in compounds with water of crystallisation, A., ii, 534.

Epps, *G. D. van*, and *Ebenezer Emmet* **Reid**, the preparation of nitriles. II. The preparation of aliphatic nitriles, A., i, 13.
  the preparation of nitriles. III. The catalytic preparations of nitriles, A., i, 13.

Ericson, *Eric John*, a new method of separating zinc from cadmium and the iodometric estimation of the latter, A., ii, 424.

Erlenmeyer, *Emil*, and *Gustav* **Hilgendorff**, the cinnamates of tartaric acid; the question of optically active cinnamic acids, A., i, 26.
Escard, *Jean*, dilatometer for measuring the absolute dilatation of liquids, A., ii, 524.
Espenhahn, *E. V.*, ammonium thiosulphate–polythionate solutions; a contribution to liquid purification of coal gas, A., ii, 310.
Essex, *J. L.* See *Nathaniel Edward* **Loomis**.
Esson, *William*, obituary notice of, T., 332.
Estes, *Clarence*, new qualitative test and colorimetric method for the estimation of vanillin, A., ii, 343.
Eto, *T.* See *Yuzuru* **Okuda**.
Euler, *Beth.* See *Hans von* **Euler**.
Euler, *Hans von*, and *Beth* **Euler**, poisoning of enzymes in the living cell, A., i, 72.
Euler, *Hans von*, and *Ernst* **Griese**, chemical composition and formation of enzymes. XIII. Alterations in the amount of enzyme in Kephir cells and in *B. lactis acidi*, A., i, 679.
Euler, *Hans von*, [with *Knut* **Haldin**], alcoholic fermentation at different concentrations of hydroxyl ion, A., i, 680.
Euler, *Hans von*, and *Harald* **Hammarsten**, the activators of fermentation, A., i, 71.
Euler, *Hans von*, and *Olof* **Svanberg**, the connexion between the metabolism of phosphates and carbohydrates in diabetes, A., i, 68.
inhibition of enzymic reactions by urine, A., i, 676.
influence of salts on solubility, A., ii, 445.
Evans, *Percy Norton*, and *J. M.* **Albertson**, the ethyl hydrogen sulphate reaction, A., i, 314.
Evans, *William Lloyd*, *W. L.* **Mong**, and *F. L.* **Sinks**, comparison of phenylhydrazine oxalate with mesoxalic acid phenylhydrazone, A., i, 595.
Evans, *Ward V.* See *John Livingston Rutgers* **Morgan**, and *John Maurice* **Nelson**.
Ewins, *Arthur James*, estimation of arsenic in organic compounds, A., ii, 101.
Ewins, *Arthur James.* See also *George* **Barger**.

F.

Faber, *Edgar M.*, and *Ebenezer Emmet* **Reid**, esterification. IX. The esterification of acetic and propionic acids by methyl, ethyl, propyl, *iso*butyl, and *iso*amyl mercaptans, A., i, 626.
Fabische. See *Max* **Cremer**.
Färber, *Eduard.* See *Carl* **Neuberg**.
Färber, *G.*, the oxidative actions of yeast, A., i, 309.
Fajans, *Kasimir*, the nomenclature of radio-elements, A., ii, 523.
the conception of the chemical element, A., ii, 566.
Fajans, *Kasimir*, and *J.* **Fischler**, the solubility of the salts of isotopic elements, A., ii, 472.
Fajans, *Kasimir*, and *M.* **Lembert**, a method for the relative atomic weight determinations of isotopic elements, A., ii, 472.
Falco, *Ferdinand.* See *Alexander* **Gutbier**.
Falconnier, *G.* See *Friedrich* **Kehrmann**.
Falk, *Kaufman George*, mode of action of urease and of enzymes in general, A., i, 182.
enzyme action. XIV. Further experiments on lipolytic actions, A., i, 598.
Falk, *Kaufman George.* See also *Kanematsu* **Sugiura**.
Faltis, *Franz*, constitution of morphine, A., i, 411.
Faltis, *Franz.* See also *Josef* **Herzig**.
Farbenfabriken vorm. *Friedrich* **Bayer & Co.**, preparation of α-methylcoumarones, A., i, 50.
preparation of 4-nitro-2-aminobenzenesulphonic [3-nitrosulphanilic] acid, A., i, 87.
preparation of ether-like derivatives of barbituric acid, A., i, 285.
preparation of 2-aminoanthraquinone and its derivatives, A., i, 463.
Farbwerke vorm. Meister, Lucius, & Brüning, preparation of bromo-α-hydroxyanthraquinones, A., i, 40.
preparation of dianthraquinonylene dioxides, A., i, 41.
preparation of mononitrocarbazoles, A., i, 53.
preparation of amino-derivatives of 2-phenylquinoline-4-carboxylic acid and its substitution products, A., i, 54.
preparation of auromercaptobenzenes, A., i, 199.
preparation of seleno-phthaleins and their halogen derivatives, A., i, 204.

Farbwerke vorm. Meister, Lucius, & Brüning, vat dyes, A., i, 225.
  preparation of arylamides of 2-hydroxynaphthalene-3-carboxylic acid, A., i, 271.
  preparation of derivatives of arsenobenzene containing nitrogen, A., i, 359.
  preparation of arylalkylhydantoins, A., i, 475.
  preparation of polychloro-substitution products of *N*-dihydro-1:2:1′:2′-anthraquinoneazine [indanthrene], A., i, 479.
Farmer, *Charles George Edgar*, obituary notice of, T., 314.
Faucon, *A.* See *Gustave* **Massol.**
Faul, *Martin.* See *Alfred* **Heiduschka.**
Feenstra, *T. P.*, a new group of antagonising atoms. I. and II., A., i, 70, 105.
Feenstra, *T. P.* See also *Hendrik* **Zwaardemaker.**
Fegely, *Walter H.* See *Richard Edwin* **Lee.**
Feigl, *Johann*, the total and residual reduction by the blood with special reference to the reducing components of the residual nitrogen; the estimation of blood-sugar under normal and pathological conditions, A., i, 64.
  the residual reduction of the blood considered in relationship to the reducing components of the residual nitrogen, A., i, 426.
  the presence of phosphates in human blood-serum. I. The phosphates soluble in acid in normal and pathological sera, A., i, 520.
Feigl, *Johann*, [with *A. V.* **Knack**, and *H.* **Koopman**], the blood of participators of an army march with accoutrements. II. Residual nitrogen and its components, blood-sugar and density, A., i, 64.
Fellenberg, *Theodore von*, various modes of combination of methyl alcohol in plants; estimation of pectin- and lignin-methyl alcohol in roots, A., i, 616.
  direct method for the estimation of starch, A., ii, 342.
  estimation of starch in clover, A., ii, 515.
Fellmer, *Ernst.* See *Hartwig* **Franzen.**
Fellner, *C.* See *Alexander* **Gutbier.**
Felty, *A. R.* See *William Allen* **Drushel.**
Fenby, *Alaric Vincent Colpoys*, apparatus for the reduction of volume of gases to standard temperature and pressure, A., ii, 37.
Fenger, *Frederic*, phosphatides in the ductless glands, A., i, 67.
Fenger, *Frederic.* See also *John Harper* **Long.**
Fenner, *Clarence N.* See *George W.* **Morey.**
Fenner, *G.*, and **Rothschild**, estimation of zinc by Schaffner's method, A., ii, 580.
Ferguson, *Allan A.* See *Alfred* **Tingle.**
Ferguson, *John*, obituary notice of, T., 333.
Ferguson, *John B.*, iodometric estimation of sulphur dioxide and the sulphites, A., ii, 267.
  estimation of iron in glass sand, A., ii, 581.
Fernandez, *R. O.*, a simple gas generator, A., ii, 255.
Fernau, *Albert*, and *Wolfgang* **Pauli**, the action of penetrating radium rays on colloids. II., A., ii, 189.
Ferry, *Edna L.* See *Thomas Burr* **Osborne.**
Fichter, *Fritz*, and *Lupu* **Glantzstein**, electrochemical chlorination of benzene and toluene, A., i, 124.
Fichter, *Fritz*, and *Max* **Schmid**, tellurium perchlorate, A., ii, 203.
Ficken, *K.* See *Heinrich* **Ley.**
Fielding, *L. E.* See *Charles Adams* **Peters.**
Filippi, *Eduardo*, yohimbine and quebrachine, A., i, 582.
  chemical and physiological detection of several alkaloids in the same solution, A., ii, 56.
Fink, *Colin Garfield*, chemical composition versus electrical conductivity, A., ii, 163.
Finkelstein, *Leo.* See *Terence T.* **Quirke.**
Fischer, *Emil*, isomerism of the polypeptides, A., i, 381.
Fischer, *Emil*, and *Max* **Bergmann**, further syntheses of glucosides by means of acetobromoglucose and quinoline; derivatives of menthol and resorcinol, A., i, 467.
  synthesis of mandelonitrile-glucoside, sambunigrin, and similar substances, A., i, 657.
Fischer, *Emil*, and *Lukas von* **Mechel**, synthesis of phenol glucosides, A., i, 216.
Fischer, *Emil*, and *Osman* **Nouri**, synthesis of phloretin, and preparation of the nitriles of phenolcarboxylic acids, A., i, 393.
  formation of hydrocoumarin derivatives (dihydro-α-benzopyrones) from phloroglucinol, A., i, 469.

Fischer, *Franz,* and *Ernst* **Baerwind,** silicon and its position in the thermoelectric series. II., A., ii, 86.

Fischer, *Franz,* and *Wilhelm* **Gluud,** optical activity of low temperature- and generator-coal tars, A., i, 258.

Fischer, *Franz,* and *Hans* **Tropsch,** the colour and oxidising value of some ozone solutions, A., ii, 463.

Fischer, *Hans,* lithofellic acid, A., i, 4.
  constitution of cotoporphyrin, A., i, 712.
  constitution of urinoporphyrin; preparation of a carboxylated hæmatic acid from urinoporphyrin, A., i, 713.

Fischer, *Martin Henry,* and *Marian O.* **Hooker,** imitation of certain anatomical structures, A., ii, 132.

Fischer, *Otto,* [with *Constanze* **Bauer**], 1:5-dihydroxynaphthalene. II., A., i, 694.

Fischer, *Otto,* [with *M.* **Chur**], action of *p*-nitroso-bases on hydrazines. II., A., i, 708.

Fischer, *Otto,* and *E.* **König,** action of phthalic anhydride on 1:6-dihydroxynaphthalene; formation of 6:6′-[3:11]-dihydroxynaphthafluoran. II., A., i, 661.

Fischer, *Ph.* See *Paul* **Pfeiffer.**

Fischler, *J.* See *Kasimir* **Fajans.**

Fishburn, *H. P.,* new type of condenser, A., ii, 305.

Fisher, *Homer G.* See *David I.* **Macht.**

Fitz, *Reginald,* and *Donald D. van* **Slyke,** acidosis. IV. Relationship between alkaline reserve and acid excretion, A., i, 522.

Fitz, *Reginald.* See also *Edgar* **Stillman.**

Fleischer, *Karl.* See *Martin* **Freund.**

Flier, *G. D.* See *Michael A.* **Rakuzin.**

Flürscheim, *Bernard Jacques,* preparation of diphenylamine, A., i, 330.

Fock, *Andreas* [*Ludwig*], the existence, size, and determination of crystal molecules, A., ii, 129.

Fodor, *Andor.* See *Emil* **Abderhalden.**

Foerster, *Fritz,* and *P.* **Dolch,** conversion of hypochlorite into chlorate in alkaline solution, A., ii, 367.

Folin, *Otto,* and *Richard D.* **Bell,** new reagent for the separation of ammonia. I. Colorimetric estimation of ammonia in urine, A., ii, 268.

Folin, *Otto,* and *E. A.* **Doisy,** impure picric acid as a source of error in the estimation of creatine and creatinine, A., ii, 159.

Folpmers, *T.,* tyrosinase, a mixture of two enzymes, A., i, 485.

Fonzes-Diacon, *Henri,* the white turbidity of wines, A., i, 373.
  the turbidity of wines, A., i, 374.

Foote, *Harry Ward,* and *Blair* **Saxton,** freezing of water absorbed in lampblack, A., ii, 241.
  effect of freezing on certain inorganic hydrogels, A., ii, 364.

Forbes, *E. B., C. E.* **Mangels,** and *L. E.* **Morgan,** a study of methods of estimation of metabolic nitrogen, A., i, 524.

Forbes, *George Shannon,* and *Herman William* **Richter,** measurement of oxidation potentials at mercury electrodes. II. The chromic-chromous potential, A., ii, 353.

Forbes, *W. E.,* a statistical study of organic series, A., ii, 292.

Formánek, *Jaroslav,* and *Josef* **Knop,** detection of phenols by the spectroscope, A., ii, 513.

Formánek, *Jaroslav, Josef* **Knop,** and *Josef* **Korber,** examination of light petroleum and benzenes, A., ii, 581.

Forster, *Aquila, Christopher* **Cooper,** and *George* **Yarrow,** compounds of ferric chloride with ethyl ether and with benzyl sulphide, T., 809; A., i, 646.

Fosse, *Robert,* origin and distribution of carbamide in nature; application of new methods of estimation of carbamide, based on the use of xanthydrol, A., i, 73.

Foster, *G. L.,* modification of the McLean-van Slyke method for the estimation of chlorides in blood, A., ii, 539.

Foster, *Henry Stennett.* See *Raphael* **Meldola.**

Foster, *William,* the action of potassium permanganate on the metals, A., ii, 175.

Foulkes, *D.,* variations of the rotatory power of galactose and dextrose in propyl alcohol at different concentrations, A., i, 79.

Fowler, *Alfred,* and (*Hon.*) *Robert John* **Strutt,** absorption bands of atmospheric ozone in the spectra of sun and stars, A., ii, 522.

Fowler, *C. C., Olaf* **Bergeim,** and *S. B.* **Hawk,** availability of certain indicators in the estimation of gastric acidity, A., ii, 49.

Fox, *John Jacob,* and *M. F.* **Barker,** estimation of phenol in commercial cresylic acid, A., ii, 513.

Fox, *Paul J.*, chemical control of ammonia oxidation, A., ii, 503.

Francis, *Arthur Gordon*, 3:4-di-*p*-nitrotetraphenylfuran, T., 1039.

Francis, *C. K.*, and *C. W.* **Crawford**, detection and estimation of sulphur in petroleum, A., ii, 379.

Franco, *S. di*, the hornblende-bearing lavas of Etna, A., ii, 498.

François, *Maurice*, stability of mercuric lactate and its aqueous solutions; preparation of mercuric lactate, A., i, 114.
  analysis of aspirin, A., ii, 224.
  estimation of antipyrine, A., ii, 226.

Frankel, *Edward M.*, enzyme action. XV. Factors influencing the proteolytic activity of papain, A., i, 597.

Franzen, *Hartwig*, and *Erling* **Aaslund**, the bromination of the two naphthylamines, A., i, 644.

Franzen, *Hartwig*, and *Ernst* **Fellmer**, methyleneamino-acids, A., i, 687.

Franzen, *Hartwig*, and *Berthold von* **Fürst**, aminohydrazines. III. *o*-Aminophenyl-β-benzylhydrazine, A., i, 58.
  aminohydrazines. IV. *p*-Acetylaminophenylhydrazine and benzylidene-*m*-aminophenylhydrazine, A., i, 59.

Franzen, *Hartwig*, and *Hubert* **Kempf**, the Bucherer reaction, A., i, 262.

Franzen, *Hartwig*. See also *Theodor* **Curtius**.

Frazer, *Joseph Christie Whitney*, *W. W.* **Holland**, and *E.* **Miller**, recovery of potassium and aluminium salts from mineral silicates, A., ii, 570.

Free, *E. E.*, symptoms of poisoning by certain elements, in pelargonium and other plants, A., i, 683.

Freed, *M.* See *Louis J.* **Curtman**.

Frenkel, *J.*, the surface electric double-layer of solid and liquid bodies, A., ii, 191.

Frerichs, *Georg*, and *E.* **Mannheim**, estimation of dextrose in urine, A., ii, 393.

Freund, *Martin*, and *Karl* **Fleischer**, [with *Eduard* **Gofferjé**, and *Johann* **Stemmer**], synthesis of indandiones. VI., A., i, 572.

Freund, *Martin*, and *Edmund* **Speyer**, thebaine. VI. Transformation of thebaine into hydroxycodeinone and its derivatives, A., i, 217.

Freundlich, *Herbert*, and *Peter* **Rona**, the sensitisation for agglutination of suspensoid colloids by non-electrolytes with capillary activity, A., ii, 365.

Freundlich, *Herbert*. See also *H.* **Dieselhorst**.

Friedberger, *E.*, and *Georg* **Joachimoglu**, the relationship between the capacity for killing and inhibiting the growth of germs and the valency, A., i, 306.

Friedemann, *Theodore E.* See *Ralph C.* **Huston**.

Friedmann, *Walter*, action of sulphur on naphthenes under pressure, A., i, 13.

Friedrich, *H.*, the nitrogenous pigments of molasses, A., i, 544.

Friedrich, *Richard*, recovery of ammonium molybdate from the filtrates obtained in the estimation of phosphorus in steel and pig-iron, A., ii, 536.

Friend, *John Albert Newton*, the effect of heat and oxidation on linseed oil, T., 162; A., i, 249.

Fromme, *Johannes*, gadolinite from the Radauthal, Harz, A., ii, 497.

Fry, *Harry Shipley*, electronic formula of benzene and molecular volumes of the chlorobenzenes, A., i, 640.

Fry, *Wm. H.* See *Edmund S.* **Shorey**.

Fuchs, *Dionys*, and *Aladár von* **Soós**, combustion of benzene in the human organism, A., i, 716.

Fühner, *Hermann*, a biological method for the estimation of choline, A., ii, 109.

Füllemann, *G.* See *Emil* **Baur**.

Fünfstück, *M.*, and *R.* **Braun**, microchemistry of Droseraceæ, A., i, 506.

Fürst, *Berthold von*. See *Hartwig* **Franzen**.

Fürst, *Rose*. See *Oskar* **Baudisch**.

Fuld, *Ernst*, the detection of blood, especially by means of malachite-green, and a new test with rhodamine, A., ii, 228.

Fulk, *M. E.* See *John James Rickard* **Macleod**.

Fuller, *Aubrey Vail*, apparatus for precipitation with hydrogen sulphide under pressure, A., ii, 464.

Funk, *Casimir*, fractionation of the phosphotungstic acid precipitate with acetone for the preparation of vitamine from yeast, A., i, 52.

G.

Gabel, *Werner*. See *Ernst* **Beckmann**.

Gabriel, *Siegmund*, bromoethylamine, A., i, 541.

Gabriel, *Siegmund*, and *Heinz* **Ohle**, *n*- and *iso*propylamine, A., i, 563.
  preparation of primary alkylamines, A., i, 565.

Gadamer, *Johannes* [*Georg*], cantharidin. VI. *iso*Cantharidin, A., i, 659.
  cantharidin. VII. Reduction products of cantharic acid and hydrobromocantharic acid, A., i, 659.
  cantharidin. VIII. Pyrogenic decomposition of barium cantharate, A., i, 704.
Gadamer, *Johannes*, [and, in part, *Walter* **Klee**], corydalis alkaloids. XIV. *r*-Corydaline, A., i, 472.
Gadamer, *Johannes*, [with *Karl* **Laske**], biological examination of honey, A., ii, 395.
Gaessler, *W. G.* See *Arthur Wayland* **Dox**.
Gaigailian, *G.* See *Siegmund* **Reich**.
Gainey, *P. L.*, the significance of nitrification as a factor in soil fertility, A., i, 529.
  effect of paraffin on the accumulation of ammonia and nitrates in the soil, A., i, 721.
Gainey, *P. L.*, and *L. F.* **Metzler**, some factors affecting nitrate-nitrogen accumulation in soil, A., i, 722.
Gale, *Hoyt S.* See *B. S.* **Butler**.
Galperin, *S.* See *E.* **Grischkevitsch-Trochimovski**.
Gangloff, *Wilmer C.*, and *William E.* **Henderson**, action of anhydrous aluminium chloride [and ferric chloride] on unsaturated organic compounds. II., A., i, 533.
Gann, *John A.*, relation between the chemical constitution of organic compounds and their capacity to coagulate acid gold hydrosols, A., ii, 21.
Gardiner, *R. F.*, and *Edmund C.* **Shorey**, the action of solutions of ammonium sulphate on muscovite, A., i, 621.
Garvin, and *A.* **Portevin**, the cooling of different metals by immersion in water, A., ii, 291.
Garvin. See also *A.* **Portevin**.
Gasser, *H. S.*, prothrombin and thrombin (free and combined) in blood serum, A., i, 426.
Gassmann, *Theodor*, estimation of selenium in bones, teeth, and urine, A., ii, 540.
Gast, *W.*, carbohydrate metabolism in the green leaf, A., i, 433.
Gattermann, *Ludwig*, and *Hans* **Schindhelm**, removal of phosphoric acid in qualitative analysis, A., ii, 41.
Gaubert, *Paul*, the circular polarisation produced by the spherolites with helicoidal winding, A., ii, 113.
  the refractive indices of rhombohedral carbonates, A., ii, 144.
  the rotatory power of liquid crystals, A., ii, 188.
Gaudion, *Georges*. See *Paul* **Sabatier**.
Gautier, [*Émile Justin*] *Armand*, an artificial soil, almost free from all mineral or organic matter, suitable for the study of plant cultures and for the examination of the influence of different fertilisers, A., i, 509.
Gautier, *Armand*, and *Paul* **Clausmann**, a new method for the destruction of tissues for the detection of arsenic and the examination of their ashes, A., ii, 421.
Gautier, *Claude*, reaction of antipyrine with *p*-dimethylaminobenzaldehyde, A., ii, 553.
Gavelin, *Axel*, högbomite, A., ii, 324.
Gawalowski, *A.*, reduction of silver chloride and lead chloride, A., ii, 88.
Geiling, *E. M. K.*, nutritive value of the diamino-acids occurring in proteins for the maintenance of adult mice, A., i, 605.
Geilmann, *W.* See *Carl* **Mannich**.
Georgeacopol, *Eugen*. See *Alfred* **Schaarschmidt**.
Gerard. See *William* **Œchsner de Coninck**.
Gerasimov, *A. F.*, preparation of collargol, A., i, 98.
  erroneous interpretation of the kinetics of chemical reactions, A., ii, 133.
Gerber, *M.*, the search for two unknown metals (neomolybdenum and neotungsten), A., ii, 575.
Geret, *L.*, colorimetric estimation of creatinine, A., ii, 225.
Gericke, *W. F.*, estimation of nitrate in the presence of chlorides, A., ii, 421.
Germann, *Albert F. O.*, and *Harold S.* **Booth**, density of silicon tetrafluoride, A., ii, 173.
Geslin, *B.* See *Jules* **Wolff**.
Gessner, *A.* See *Johannes* **D'Ans**.
Getman, *Frederick Hutton*, action of magnesium on solutions of potassium chloride, A., ii, 90.
  action of magnesium on aqueous solutions, A., ii, 258.
  allotropy of cadmium, A., ii, 533.
Gettler, *Alexander O.*, [with *Ruth* **Oppenheimer**], factors involving the accuracy of creatinine estimations in human blood, A., ii, 184.
Gewecke, *Julius*, electroanalysis using silvered glass basins in place of platinum cathodes, A., ii, 334.
Ghosh, *Jnanendra Chandra*, the discharge potentials of ions on heated electrodes. I., A., ii, 352.
  a new method of preparing colloids, A., ii, 563.

Ghosh, *Jnanendra Chandra*. See also *Prafulla Chandra* **Rây**.

Ghosh, *Praphulla Chandra*, action of acetaldehyde-ammonia on quinones, T., 608; A., i, 517.

Ghosh, *Praphulla Chandra*, and *Edwin Roy* **Watson**, effect of additional auxochromes on the colour of dyes. II. Triphenylmethane- and azo-dyes, T., 815; A., ii, 523.

Ghosh, *Sudhamoy*, the sublimation of sugars, A., i, 80.

Ghosh, *Sudhamoy*. See also *John Edwin* **Mackenzie**.

Gianoli, *Giuseppe*, preparation of hydrogen from formates and from carbon monoxide, A., ii, 85.

Gibbons, *Willis A.*, heat of dilution of alcohol in benzene, A., ii, 164.

Gibson, *Charles Stanley*, *John Lionel* **Simonsen**, and *Madyar Gopala* **Rau**, [with *John Edward* **Purvis**], the nitration of 2-acetylamino-3:4-dimethoxybenzoic acid and 3-acetylaminoveratrole, T., 69; A., i, 203.

Gillespie, *Louis J.*, and *E. H.* **Walters**, the possibilities and limitations of the Duclaux method for the estimation of volatile acids, A., ii, 549.

Gillett, *Horace Wadsworth*, emulsions and suspensions with molten metals, A., ii, 80.

Giua, *Michele*, aromatic nitro-derivatives. VI. General considerations, A., i, 18.
  mixtures of nitrated explosives. II., A., i, 19.
  action of oxalyl chloride on ethers of the naphthols, A., i, 204.
  molecular organic compounds, A., i, 386.
  an ethoxy-β-naphthoylpropionic acid, A., i, 394.
  action of furfuraldehyde on cinnamylidenemethyl methyl ketone, A., i, 408.

Givens, *Maurice Hope*, Benedict's method for the estimation of total sulphur in urine, A., ii, 180.
  calcium and magnesium metabolism. II. Effect of diets poor in calcium. III. Effect of fat and fatty acid derivatives, A., i, 603.

Givens, *Maurice Hope*, and *Lafayette Benedict* **Mendel**, calcium and magnesium metabolism. I. Effects of alkali and acid, A., i, 603.

Glantzstein, *Lupu*. See *Fritz* **Fichter**.

Glenck, *Otto von*. See *Fritz* **Ullmann**.

Gluud, *Wilhelm*. See *Franz* **Fischer**.

Godchot, *Marcel*. See *Georges* **Charpy**.

Goddard, *Win R.* See *Stewart Woodford* **Young**.

Godet, *Ch.* See *W. I.* **Baragiola**.

Godfrin, *P.*, detection of ovalbumin in urine, A., ii, 59.
  criticism of the method of detecting urinary albumin by heat; new process permitting the detection of the smallest traces of albumin in urine, A., ii, 59.

Godon, *F. de*. See *Alphonse* **Mailhe**.

Goerens, *Franz*. See *Rudolf* **Ruer**.

Görgey, *R.*, zeolites from Neubauerberg, Leipa, Bohemia, A., ii, 493.

Gofferjé, *Eduard*. See *Martin* **Freund**.

Goldberg, *Alfred*. See *Theodor* **Curtius**.

Goldberg, *Alwin* [*Heinrich*], *p*-nitrophenol as an indicator in water-analysis, A., ii, 498.

Goldschmidt, *Victor Moritz*, the crystalline form of phenylglyceric acid and its active components, A., i, 561.

Goldstein, *Eugen*. See *Alfred* **Heiduschka**.

Gomberg, *Moses*, and *Oliver* **Kamm**, tetraphenylmethane, A., i, 642.

Gomberg, *Moses*, and *C. S.* **Schoepfle**, triphenylmethyl. XXVII. Molecular weights of the triarylmethyls, A., i, 551.

Gonnermann, *Max*, biochemistry of silicic acid, A., i, 494.

Gooch, *Frank Austin*, and *Matsusuke* **Kobayashi**, electrolytic analysis with small platinum electrodes, A., ii, 334.
  use of the platinised anode of glass in the electrolytic estimation of manganese, A., ii, 425.

Gordon, *M. H.*, nitrogenous food requirement of some of the commoner pathogenic bacteria, A., i, 528.

Gortner, *Ross Aiken*, the organic matter of the soil. II. A study of carbon and nitrogen in seventeen successive extracts; with some observations on the nature of the black pigment of the soil, A., i, 248.
  the organic matter of the soil. I. Some data on humus, humus carbon, and humus nitrogen, A., i, 310.
  the organic matter of the soil. III. The production of humus from manures, A., i, 311.

Gortner, *Ross Aiken*, and *William M.* **Shaw**, the organic matter of the soil. IV. Some data on humus-phosphoric acid, A., i, 376.

Gortner, *Ross Aiken*, and *Alexander J.* **Wuertz**, comparative analyses of fibrin from different animals, A., i, 711.

Gortner, *Ross Aiken*. See also *Clarence Austin* **Morrow**.

Goss, *B. C.*, inhibition of digestion of proteins by adsorbed tin, A., i, 497.
  production of light at low temperatures by catalysis with metal and metallic oxide hydrosols, A., ii, 436.
Gott, *E. J.* See *Philip Lee* **Blumenthal**.
Gounder, *A.* See *Georgi* **Korschun**.
Gouy, *G.*, the electro-capillary function, A., ii, 291.
Graber, *Howard T.*, rennin, A., ii, 60.
  a résumé of tests for pepsin, A., ii, 60.
Graefe, *Edmund*, use of Shukov's apparatus for molecular weight determinations, A., ii, 441.
Graff, *H. C. de*, biochemical properties of paratyphus bacilli, A., i, 306.
Graham, *J. J. T.* See *C. C.* **McDonnell**.
Grandjean, *Francis*, orientation of anisotropic liquids on crystals, A., ii, 451.
Grant, *A. J.*, and *Charles* **James**, some rare earth compounds, A., ii, 316.
Grasser, *Georg*, chemical investigation of the substance of the birch, A., i, 437.
Graves, *Sara Stowell*, and *J. T. W.* **Marshall**, [with *H. W.* **Eckweiler**], leucine anhydride, a product of the hydrolysis of protein by water at high temperatures, A., i, 358.
Gray, *George P.*, and *A. W.* **Christie**, a boiling method for the estimation of water-soluble arsenic in lead arsenate, A., ii, 102.
Gray, *Harold Heath*, a simple apparatus for the washing of gases, T., 179; A., ii, 198.
Greaves, *Joseph James*, influence of salts on the bacterial activities of the soil, A., i, 243.
Greaves, *Joseph James*, and *C. T.* **Hirst**, some factors influencing the estimation of nitric nitrogen in the soil, A., ii, 578.
Green, *Arthur George*, and *Frederick Maurice* **Rowe**, conversion of *o*-nitroamines into *iso*oxadiazole oxides, and of *o*-nitrosoamines into *iso*oxadiazoles, T., 612; A., i, 518.
Green, *Helen S.* See *Anna E.* **Richardson**.
Greenwald, *Isidor*, non-protein nitrogen of blood: 1. Removal of the protein. 2. Estimation of creatine, A., i, 523.
Greenwald, *Isidor*, and *Morris L.* **Weiss**, fate of inositol administered to dogs, A., i, 610.
Greenwell, *Allan*. See *Richard Vernon* **Wheeler**.
Gregg, *E. T.*, improved compensator for gas analysis, A., ii, 379.
Grekova, (*Mlle.*) *E. A.* See *S. S.* **Nametkin**.
Grey, *Egerton Charles*, the estimation of succinic acid, A., ii, 517.
Griesbach, *Walter*, and *H.* **Strassner**, residual reducing power of the blood, A., i, 491.
Griese, *Ernst*. See *Hans von* **Euler**.
Griffith, *Robert Owen*, *Alfred* **Lamble**, and *William Cudmore McCullagh* **Lewis**, studies in catalysis. VI. The mutual influence of two reactions proceeding in the same medium, T., 389; A., ii, 302.
Griffiths, *A.*, calculation of the coefficient of diffusion of a salt at a definite concentration, A., ii, 294.
Griffiths, *John*, obituary notice of, T., 317.
Grimbert, *Léon*, detection of cryogenine in urine, A., ii, 344.
Grimm, *F.* See *Richard* **Stoermer**.
Grimmer, *Joseph*. See *Paul* **Pfeiffer**.
Grinberg, (*Mlle.*) *R.* See *Alex. P.* **Orechov**.
Grischkevitsch-Trochimovski, *E.*, sulphides with four-membered rings, A., i, 153.
  hexamethylene sulphide, A., i, 157.
  rupture of the ring of cyclic sulphides, A., i, 157.
  behaviour of dihalogenated compounds towards alkali sulphides; general characteristics of the sulphides formed, A., i, 158.
Grischkevitsch-Trochimovski, *E.*, [with *O.* **Cykina**], sulphides with six-membered rings, A., i, 156.
Grischkevitsch-Trochimovski, *E.*, [with *L.* **Nekritsch**, and *S.* **Galperin**], sulphides with five-membered rings, A., i, 154.
Gröppel, *H.*, the analysis of coal, and a new scheme for the examination of coal, A., ii, 384.
Groll, *J. Temminck*, periodic phenomena shown by ferments, A., i, 425.
Groschuff, *Eric*. See *Franz* **Mylius**.
Grossfeld, *Johannes*. See *C.* **Baumann**.
Grossmann, *Hermann*, and *Julie* **Mannheim**, α-benzildioxime [reagent for nickel], A., ii, 391.
  separation of nickel and copper by means of dimethylglyoxime, A., ii, 512.
Grosspietsch, *O.*, apatite from Sunk, Styria, A., ii, 489.
Groth, *P.*, the relation between chemical constitution and crystal structure, A., ii, 446.
Gruber, *Josef*. See *Anton* **Skrabal**.
Grün, *Adolf*, and *E.* **Ulbrich**, Montan wax, A., i, 5.
Grün, *Adolf*. See also *G.* **Schicht**.

Grünstein, *N.*, preparation of aldol, A., i, 686.

Grüttner, *Gerhard*, and *Erich* **Krause,** new heterocyclic systems. III. Organo-lead compounds. IV. Diethyl*cyclo*pentamethyleneplumbine and products obtained by rupturing the ring, A., i, 122.

resistance of the alkyl groups attached to a lead atom to the disruptive action of halogens; preparation of mixed lead alkyls containing three or four different radicles, A., i, 256.

organo-lead compounds. VI. Lead tetra*iso*amyl, lead tetra*iso*butyl, lead tetra-*n*-propyl, and their derivatives, A., i, 257.

organo-lead compounds. VII. Lead tetra-alkyls with secondary alkyl radicles, and their behaviour towards halogens, A., i, 384.

Gruse, *W. A.*, and *Solomon Farley* **Acree,** reactions of both the ions and the molecules of acids, bases, and salts; the inversion of menthone by sodium, potassium and lithium ethoxides, A., ii, 251.

Gruzit, *Oswald M.*, the effect of some acids and alkalis on soil bacteria in the soil solution, A., i, 430.

Günther, *Paul*, electromotive behaviour of lead, A., ii, 439.

Guerbert, *Marcel*, condensation, under the influence of potassium hydroxide, of *cyclo*hexanol with *iso*propyl alcohol; synthesis of *cyclo*hexyl*iso*propyl alcohol, A., i, 453.

condensation, under the action of potassium hydroxide, of *cyclo*hexanol with *sec.*-butyl alcohol; synthesis of α-*cyclo*-hexylbutan-β-ol, A., i, 694.

Guggenheim, *Markus*, the active principle of the pituitary gland, A., i, 526.

Guglialmelli, *Luis*, a new reaction distinguishing the sugars, A., ii, 276.

a general method for the detection of phenols in essential oils, A., ii, 514.

identification of the naphthols; a new and delicate test for α-naphthol, A., ii, 547.

Guglialmelli, *Luis*, and *Ulaus* **Hordh,** estimation of tungstic acid in wolframite, A., ii, 545.

Guichard, *Marcel*, a new method of determining the atomic weight of iodine, A., ii, 201.

Guillaume, *Charles Édouard*, changes in the expansion of alloys of iron and nickel under the action of different thermal or mechanical treatments, A., ii, 356.

Gulbransen, *R.* See *Carl Hamilton* **Browning.**

Gulf Refining Co., preparation of glycols, A., i, 377.

Gupta, *N. M.* See *Morris William* **Travers.**

Gurvitsch, *L. G.*, physico-chemical force of attraction. III., A., ii, 123.

theory of heterogeneous catalysis, A., ii, 136.

Gutbier, *Alexander*, and *C.* **Fellner,** a new class of palladium compounds; palladous trichlorides and tribromides, A., i, 542.

Gutbier, *Alexander*, and *C.* **Fellner,** [with *J.* **Kräuter,** *Ferdinand* **Falco,** *A.* **Krell,** *Fr.* **Schulz,** and *M.* **Woernle**], palladium, A., i, 541.

Gutbier, *Alexander*, and *A.* **Hüttlinger,** rhodium, A., ii, 482.

Gutbier, *Alexander*, *A.* **Hüttlinger,** and *O.* **Maisch,** the action of oxygen on rhodium, A., ii, 483.

Gutbier, *Alexander*, and *Nora* **Kräutle,** protective colloids. VIII. *Tubera salep* as protective colloid. I. General colloido-chemical investigation of salep extract, A., ii, 244.

protective colloids. VIII. *Tubera salep* as protective colloid. II. Colloidal silver, A., ii, 298.

protective colloids. VIII. *Tubera salep* as protective colloid. III. Colloidal arsenic, A., ii, 298.

protective colloids. VIII. *Tubera salep* as protective colloid. IV. Colloidal antimony, A., ii, 299.

Gutbier, *Alexander*, [with *G. A.* **Leuchs,** and *H.* **Wiessmann**], the oxides of ruthenium, A., ii, 483.

Gutbier, *Alexander*, *G. A.* **Leuchs,** *H.* **Wiessmann,** and *O.* **Maisch,** the action of oxygen on ruthenium, A., ii, 38.

Gutbier, *Alexander*, and *A.* **Wagner,** protective colloids. VII. *Cydonia* seed as protective colloid. I., A., ii, 131.

protective colloids. VII. *Cydonia* seed as protective colloid. II. Colloidal silver, A., ii, 168.

protective colloids. VII. *Cydonia* seed as protective colloid. III. Colloidal gold, A., ii, 169.

protective colloids. VII. *Cydonia* seed as protective colloid. IV. Colloidal mercury, A., ii, 169.

protective colloids. VII. *Cydonia* seed as protective colloid. V. Colloidal platinum, A., ii, 169.

Gutbier, *Alexander*, and *G. L.* **Weise,** protective colloids. VI. *Radix althaeae* as protective colloid, A., ii, 21, 131.

Guye, *Charles Eugène*, and *C.* **Stanescu**, the explosive potential in carbonic anhydride at high pressures, A., ii, 231.
  disruptive discharge in compressed gases, A., ii, 231.

Guye, *Philippe Auguste*, the latest revisions of the international table of atomic weights, A., ii, 198.
  general considerations relative to the physico-chemical revision of the atomic weight of bromine on the basis of the normal density of gaseous hydrogen bromide, A., ii, 199.
  the faulty values of the atomic weights of carbon and sulphur, A., ii, 257.
  volumetric relationship of the combination of hydrogen and oxygen, $2H_2:O_2$, and the atomic weight of hydrogen, A., ii, 412.

Guzmán Carrancio, *Julio de*, and *P.* **Poch**, electroanalysis of zinc and cadmium without platinum electrodes, A., ii, 509.

Gyzander, *C. R.*, titration of sulphuric acid, A., ii, 39.

H.

Haar, *Anne Wilhelm van der*, the chemistry of the saponins, A., i, 41.
  the pharmacology of saponins, A., i, 70.
  formation of *m*-nitrophenylhydrazine from *m*-nitroaniline by Bischler and Brodsky's method, A., i, 228.
  ivy-peroxydase, a gluco-protein, and G. Woker's aldehyde-hypothesis of the peroxydases, A., i, 301.
  new hydrazones of some monosaccharides (*p*-tolylhydrazones of *l*-arabinose, rhamnose, fucose, *d*-mannose, and *d*-galactose), A., i, 380.
  o-tolylhydrazine, a new characteristic and sensitive reagent for *d*-galactose, A., ii, 515.

Haas, *A.*, the positive nucleus of the atom, A., ii, 528.

Haas, *A. R.*, a simple and rapid method of studying respiration by the detection of exceedingly minute quantities of carbon dioxide, A., i, 433.

Haas, *Ph. C. Wladislaw*, rhodium catalysis of formic acid, A., ii, 136.

Habasian, *Y.* See *Ebenezer Henry* **Archibald.**

Hadfield, (*Sir*) *Robert*, and *Edgar* **Newbery**, the corrosion and electrical properties of steels, A., ii, 210.

Hadley, *Sidney E.* See *Treat Baldwin* **Johnson.**

Haensler, *Paul.* See *Adolf* **Kaufmann.**

Haff, *R. C.*, and *E. H.* **Schwartz**, cobaltinitrite method for the estimation of potassium, A., ii, 507.

Haftka, *J.* See *Oscar* **Baudisch.**

Hager, *G.*, and *J.* **Kern**, estimation of dicyanodiamide in nitrolime, A., ii, 518.

Hagmaier, *E. W.*, analysis of babbit metal and alloys of tin, antimony, lead, and copper, A., ii, 181.

Hahn, *Dorothy A.* See *Treat Baldwin* **Johnson.**

Hahn, *Erna.* See *Paul* **Ehrenberg**, and *Otto* **Nolte.**

Hahn, *Friedrich L.*, the course of the reaction between silver and sulphides (Hepar test), A., ii, 371.
  a precipitant for nitrous acid, A., ii, 382.
  the estimation of copper as sulphide and by electrolysis, A., ii, 543.

Hahn, *L.*, and *S.* **Kyropoulos**, alloys of manganese with gold, A., ii, 476.

Haigh, *Frank Loyal.* See *William Gilbert* **Mixter.**

Halberkann, *Josef*, occurrence of ψ-cubebin in *Ocotea usambarensis*, Engl., A., i, 507.

Haldin, *Knut.* See *Hans von* **Euler.**

Hale, *Harrison*, and *W. L.* **Hartley**, method of extraction as affecting the estimation of phosphoric acid in soils, A., ii, 41.

Hale, *William Jay*, the *cyclo*pentadiene series. IV. The formation of *cyclo*pentadienedihydropyridazines, A., i, 55.

Hall, *Frank*, vacuum-jacketed pyknometer for liquids, A., ii, 442.

Hall, *Norris Folger*, drainage of crystals, A., ii, 363.
  periodicity among the radioactive elements, A., ii, 438.

Hall, *Norris Folger.* See also *Theodore William* **Richards.**

Hall, *Ralph E.*, and *William Draper* **Harkins**, free energy of dilution and the freezing-point lowerings in solution of some salts of various types of ionisation, and of salt mixtures, A., ii, 65.

Hall, *Ralph E.* See also *William Draper* **Harkins.**

Haller, *Albin*, and (*Mme.*) *Pauline* **Ramart-Lucas**, syntheses by means of sodamide. V. Preparation of δ-aminoketones and of 2-phenyl-3:3-dialkyltetrahydropyridines, A., i, 665.

Haller, *R.*, colloidal ferric ferricyanides, A., i, 324.

Haller, *R.*, the micellary theory of Nägeli as a working hypothesis in the investigation of chemical and physical changes in cotton fibres, with special reference to the processes of dyeing, A., i, 436.

Hallett, *R. L.*, the volumetric estimation of tin, A., ii, 46.

Halliburton, *William Dobinson*, and *Jack Cecil* **Drummond,** nutritive value of margarines and butter substitutes with reference to their content of the fat-soluble accessory growth substance, A., i, 673.

Halse, *O. M.*, and *Herman* **Dedichen,** the turpentine obtained during the sulphate-cellulose process, A., i, 398.

Halse, *O. M.* See also *Eyvind* **Bœdtker.**

Hamburger, *L.*, and *W.* **Koopman,** analysis of very small quantities of gas, A., ii, 500.

Hamburger, *L.* See also *Willem* **Reinders.**

Hamburger, *Toni*, diffusion and osmosis under the influence of electro-capillary forces, A., ii, 562.

Hammarsten, *Einar*, the synthesis of amino-acids; α-amino-γδ-dihydroxyvaleric acid; γ-hydroxyproline; αδ-diamino-γ-hydroxyvaleric acid, A., i, 81.

Hammersten, *Harald.* See *Hans von* **Euler.**

Hammick, *Dalziel Llewellyn*, action of sulphur dioxide on metal oxides. I., T., 379; A., ii, 306.
  the oxy-ammonia flame, A., ii, 85.

Hanck, *Paul*, electrolysis of hydrochloric acid, A., ii, 462.

Hankin, *Ernest Hanbury*, tests for certain narcotic and anæsthetic drugs, A., ii, 184.

Hantzsch, *Arthur* [*Rudolf*], the supposed keto-enol isomerism of ethyl succinylsuccinate and ethyl *p*-dihydroxyterephthalate, A., i, 685.
  chromoisomerism of acridinium salts, A., i, 708.

Hanzlik, *Paul J.* See *R. W.* **Scott.**

Harden, *Arthur*, conditions of activation of washed zymin and the specific function of certain cations in alcoholic fermentation, A., i, 501.

Harden, *Arthur*, and *Sylvester Solomon* **Zilva,** alleged antineuritic properties of 2-hydroxypyridine and adenine, A., i, 612.

Harding, *T. S.* See *Claude S.* **Hudson.**

Harding, *Victor John*, alleged ninhydrin reaction with glycerol, etc., A., ii, 275.

Harding, *Victor John*, and *Edward H.* **Mason,** estimation of chlorides in body fluids, A., ii, 501.

Hári, *Paul*, the absorption of light by oxyhæmoglobin, A., i, 597.

Harker, *George*, [approximate] estimation of toluene and benzene in coal-tar oils, A., ii, 338.

Harkins, *William Draper*, evolution of the elements and the stability of complex atoms; a new periodic system which shows a relation between the abundance of the elements and the structure of the nuclei of atoms, A., ii, 303.

Harkins, *William Draper*, *F. E.* **Brown,** and *Earl C. H.* **Davies,** surface tension. V. Structure of the surfaces of liquids, and solubility as related to the work done by the attraction of two liquid surfaces as they approach each other, A., ii, 238.

Harkins, *William Draper*, *Earl C. H.* **Davies,** and *George L.* **Clark,** surface tension. VI. Orientation of molecules in the surfaces of liquids; energy relations at surfaces, solubility, adsorption, emulsification, molecular association, and the effect of acids and bases on interfacial tension, A., ii, 239.

Harkins, *William Draper*, *Ralph E.* **Hall,** and *W. A.* **Roberts,** cobaltammines. I. Various ionisation types as determined by the freezing-point lowering in aqueous solution, together with conductivity measurements, A., ii, 94.

Harkins, *William Draper*, and *Harry M.* **Paine,** effect of salts on the solubility of other salts. VIII*a*. The solubility relations of a very soluble bi-univalent salt, A., ii, 75.

Harkins, *William Draper*, and *W. Tudor* **Pearce,** effect of salts on the solubility of other salts. VIII*b*. Solubility relations of some extremely soluble salts, A., ii, 76.
  ionisation and solubility relations of salts of higher types. IV. Intermediate ions in solutions of unibivalent salts, and of lanthanum iodate, a ter-univalent salt, A., ii, 77.

Harkins, *William Draper*, and *W. A.* **Roberts,** freezing-point lowerings in aqueous solutions of salts and mixtures of salts, and of a salt with a non-electrolyte, A., ii, 66.

Harkins, *William Draper.* See also *Ralph E.* **Hall.**

Harned, *Herbert S.*, titration of some bivalent metal sulphates by the conductance method, A., ii, 272.
Harries, *Carl Dietrich*, action of ozone on inorganic compounds, A., ii, 464.
Harries, *Carl Dietrich*, [with *Kurt* **Oppenheim,** *Heinrich* **Neresheimer,** *Hans von* **Splawa-Neyman,** *Robert Viner* **Stanford,** and *Edgar* **Paulsen**], ozone and its action on organic compounds, A., i, 210.
Harris, *Ben R.* See *Louis J.* **Curtman.**
Harris, *David Fraser*, colourless crystals of hæmoglobin, A., i, 64.
Harris, *J. E.*, adsorption by soils, A., ii, 443.
Harrison, *William*, relation between the colour and the degree of dispersion of particles in coloured solutions, A., ii, 131.
Hart, *Edward*, preparation of sulphurous acid, A., ii, 256.
  glauconite or greensand, A., ii, 537.
Hart, *Edwin Bret*, and *George Colvin* **Humphrey,** [with *Barnett* **Sure**], relation of the quality of proteins to milk production. III., A., i, 608.
Hart, *Edwin Bret*, and *Barnett* **Sure,** influence of carbohydrates on the accuracy of the van Slyke method in the hydrolysis of caseinogen, A., ii, 111.
Hart, *Edwin Bret.* See also *Barnett* **Sure.**
Hart, *Merrill C.*, and *Frederick William* **Heyl,** some constituents of jambul, A., i, 191.
Hartley, *Ernald George Justinian*, some reactions produced by mercuric iodide, A., i, 82.
  the reaction between methyl iodide and some metallic cyanides, A., i, 83.
Hartley, *W. L.* See *Harrison* **Hale.**
Hartmann, *A.*, the internal field of the lithium atom, A., ii, 206.
Hartung, *E. J.*, the theory of solution, A., ii, 445.
Harvey, *E. Newton*, bioluminescence. II. Luciferin in luminous bacteria. III. Action of oxydases, A., i, 365.
  bioluminescence. IV. In *Cypridina hilgendorfii* (Japanese ostracod crustacean). V. In firefly. VI. In *Cavernularia haberi* (Japanese pennatulid), A., i, 365.
  bioluminescence. VIII. Mechanism of the production of light during the oxidation of pyrogallol, A., ii, 436.
Hasselbalch, *Karl Albert*, the true nature of the "acidotic condition" of infants, A., i, 425.
  the calculation of the hydrion concentration of the blood from the amount of its free and bound carbon dioxide, and the combination of the blood with oxygen considered as a function of the hydrion concentration, A., i, 490.
  the hydrogen number and oxygen-combining power of the blood, A., i, 601.
Hasselt, *J. F. B. van.* See *Inne Jan* **Rinkes.**
Hassreidter, *V.*, estimation of zinc by Schaffner's method, A., ii, 509.
Hastings, *J. H.*, estimation of zinc, A., ii, 333.
Hatcher, *W. H.*, and *Frederick William* **Skirrow,** the compounds of phenol and the cresols with pyridine, A., i, 665.
Hatschek, *Emil*, the theory of gels as systems of two liquid phases, A., ii, 451.
Hauser, *Enrique*, a new industrial apparatus for the estimation of combustible gases, A., ii, 266, 338.
Hausmann, *Walther*, the sensitising action of the natural porphyrins, A., i, 69.
Haward, *William Arthur*, and *Sosale Garalapury* **Sastry,** the uniform movement of flame in mixtures of acetylene and air, T., 841; A., ii, 527.
Hawes, *W. C.* See *O. L.* **Barnebey.**
Hawick, *Christina M.* See *Harry* **Rainy.**
Hawk, *S. B.* See *C. C.* **Fowler.**
Hawkins, *Lon A.*, utilisation of certain pentoses and compounds of pentoses by *Glomerella cingulata*, A., i, 503.
Hawley, *F. G.*, accurate estimation of silica in commercial analysis, A., ii, 332.
Haworth, *Walter Norman*, and *James* **Law,** constitution of the disaccharides. I. Structure of sucrose, A., i, 80.
Haynes, (*Miss*) *Dorothy.* See *Samuel Barnett* **Schryver.**
Haynes, *W. G.*, handling a standard solution of barium hydroxide, A., ii, 327.
Healy, *D. J.* See *Philip Lee* **Blumenthal.**
Hébert. See **Villedieu.**
Hedvall, *J. Arvid*, the determination of dissociation temperatures with the aid of cooling and heating curves, especially for cobalto-cobaltic oxide, A., ii, 15.
  the formation of cobalt aluminate, cobalt orthostannate, and Rinman's green, A., ii, 35.

Hedvall, *J. Arvid,* the reactivity of silica with the oxides of calcium, barium, and magnesium in the solid state, A., ii, 205.
the temperatures of formation and decomposition of the carbonates of calcium, strontium, barium, and magnesium under a pressure of one atmosphere, A., ii, 208.

Heidelberger, *Michael.* See *Walter Abraham* **Jacobs.**

Heider, *K.* See *Julius von* **Braun.**

Heiduschka, *Alfred,* direct estimation of chlorine in urine by the modified Volhard's method, A., ii, 38.

Heiduschka, *Alfred,* and *Martin* **Faul,** colorimetric methods for the estimation of very small quantities of morphine, A., ii, 554.

Heiduschka, *Alfred,* and *Eugen* **Goldstein,** product of oxidation of *p*-phenylenediamine (ursol) by hydrogen peroxide; (Bandrowski's base, tetra-amino-di-phenyl-*p*-azophenylene), A., i, 482.

Heiduschka, *Alfred,* and *A.* **Panzer,** bixin, A., i, 408.

Heiduschka, *Alfred,* and *H.* **Sieger,** solanine, A., i, 407.

Heiduschka, *Alfred,* and *H.* **Zirkel,** action of formaldehyde on lactose, maltose, and sucrose, A., i, 446.

Heim, *R.* See *B.* **Stuber.**

Heine, *Hermann.* See *Gustav* **Heller.**

Heinemann, *Arthur,* preparation of nitro-compounds, A., i, 126.

Heise, *George W.,* and *Amando* **Clemente,** stripping and analysis of galvanised iron, A., ii, 336.
detinning and analysis of tin plate, A., ii, 337.

Heise, *George W.* See also *J. R.* **Wright.**

Hekma, *Ebel,* fibrin and its relationship to problems of biology and colloidal chemistry; the problem of blood coagulation. X. The micellar crystalline character of fibrin, A., i, 101.
fibrin excretion under the influence of an electric current, A., i, 361.
specific behaviour of proteins, A., i, 420.
fibrin and its relationship to certain questions in biology and the chemistry of colloids. X. The two kinds of fibrin sols and their relations to the conceptions of colloidal solutions, A., ii, 22.
fibrin in its relationship to certain questions in biology and the chemistry of colloids. XI. The three kinds of fibrin gels, A., ii, 23.

Helderman, *Willem Dirk.* See *Hugo Rudolph* **Kruyt.**

Heller, *Gustav,* new cases of isomerism, A., i, 219.
synthesis of a crystalline 2-*iso*curcumin, A., i, 705.
constitution of isatin salts, A., i, 708.
dindole, A., i, 708.

Heller, *Gustav,* [with *Hermann* **Heine**], oxindole, A., i, 220.

Heller, *Robert,* bioluminescence and metabolism, A., i, 427.

Hembrough, *E.* See *Henry Droop* **Richmond.**

Hemmelmayr [von Augustenfeld], *Franz [Josef],* preparation of 1:5-dihydroxynaphthalenedicarboxylic acid, A., i, 457.
the influence of the solvent on the reaction between polyhydric phenols and alkali hydrogen carbonates, A., i, 645.

Hemmerlé, (*Mlle.*) *R.,* phenylpyruvic acid, A., i, 394.

Hempel, *Stanislas.* See *Friedrich* **Kehrmann.**

Hemsalech, *Gustave Adolphe,* the groups of rays of iron under the selective influence of thermal and chemical actions, A., ii, 61.
origin of the line spectrum emitted by iron vapour in the explosion region of the air-coal-gas flame, A., ii, 521.
production of coloured flames of high luminosity for demonstration and experimental purposes, A., ii, 523.

Henderson, *G. H.,* initial charged condition of the active deposits of radium, thorium, and actinium, A., ii, 351.

Henderson, *William E.* See *Wilmer C.* **Gangloff.**

Henderson, *William Roland,* and *Hugh Stott* **Taylor,** neutral salt action on acid solubilities, A., ii, 77.

Henderson, *Yandell,* and *W. H.* **Morriss,** applications of gas analysis. I. Estimation of carbon dioxide in alveolar air and blood, and the carbon dioxide combining power of plasma, and of whole blood, A., ii, 506.

Henriques, *Valdemar,* and *E.* **Christiansen,** the ammonia content of the blood, A., i, 425, 491.

Herdt, *A.* See *N.* **Tschischevsky.**

Hering, *Carl,* elements neither free nor combined; a third state, A., ii, 460.

Herovici, *L.* See *Hugo* **Simonis.**

Herrmann, *A.,* simple method of estimating the contents of sozoiodol-mercury preparations, A., ii, 399.

Herrmann, *A.* See also *Erwin* **Rupp.**

Herstad, *O.*, the action of mercuric chloride on gold hydrosols, A., ii, 168.

Herwig, *With.*, estimation of chromium in ferrochrome, A., ii, 104.

Herz, *Walter* [*Georg*], the ratio of the boiling-point to the critical temperature, **A.**, ii, 14.
  internal friction of chlorinated aliphatic hydrocarbons, A., ii, 194.
  diameter (of molecules) and solubility, A., ii, 195.
  two rules on the connexion between some physical properties of homologous series of organic compounds, A., ii, 236.
  the internal friction of aqueous salt solutions, A., ii, 361.
  the Guldberg and Trouton-Nernst rules in homologous series of compounds, A., ii, 441.

Herzbaum, *Alexander*. See *Friedrich* **Kehrmann.**

Herzfeld, *E.*, and *R.* **Klinger**, the chemistry of the proteins, A., i, 300.
  the chemistry and physiology of the coagulation of the blood. III., A., i, 671.

Herzig, *Josef*, and *Franz* **Faltis**, bixin, A., i, 577.

Herzig, *Josef*, and *Franz* **Wenzel**, [with *St.* **Eberwein**], tetra- and penta-methylorcinol. II., A., i, 133.

Herzig, *Josef*, and *Franz* **Wenzel**, [with *E.* **Taigner**, and *A.* **Kichler**], the hydrolysis of methyl-*tert.*-butyl- and dimethyl-*tert.*-butyl-triaminobenzene, A., i, 176.

Hess, *Kurt*, degradation of scopoline, A., i, 52, 162.
  the alkaloids of the pomegranate tree. I. Pelletierine, A., i, 349.

Hess, *Kurt*, and *K.* **Dorner**, alkyl ethers of benzaldehydecyanohydrin. I., A., i, 337.

Hess, *Kurt*, and *A.* **Eichel**, alkaloids of the pomegranate tree. II. Tanret's methylpelletierine and Piccinini's *iso*methylpelletierine, A., i, 350.

Hess, *Kurt*, *A.* **Eichel**, and *Cl.* **Uibrig**, action of aldehydes on hydramines of the pyrrolidine and piperidine series. V. Scission of tertiary methylaminoketones into formaldehyde and secondary hydramine bases, A., i, 352.

Hess, *Kurt*, and *F.* **Leibbrandt**, methylation of cyclic amino-acids. II. Synthesis of 1-methylhexahydropicolinic and 1-methylhexahydronicotinic acids, A., i, 354.

Hess, *Kurt*, and *Cl.* **Uibrig**, glyoxal, A., i, 319.

Hess, *Kurt*, *Cl.* **Uibrig**, and *A.* **Eichel**, action of aldehydes on hydramines of the pyrrolidine and piperidine series. IV. A method for alkylating secondary amino-alcohols, A., i, 351.

Hesse, [*Julius*] *Oswald*, chrysarobin. III., A., i, 276.
  lichens and their characteristic constituents. XV., A., i, 457.

Heublein, *O.* See *Josef* **Tillmans.**

Hewlett, *Mary.* See *Samuel Barnett* **Schryver.**

Heyl, *Frederick William*, analysis of ragweed pollen, A., i, 618.

Heyl, *Frederick William.* See also *Merrill C.* **Hart.**

Heyn, *Albrecht*, estimation of hardness in water, A., ii, 218.

Heyn, *Myron.* See *Heinrich* **Biltz.**

Hibbard, *P. L.*, estimation of potassium; the Lindo-Gladding method, A., ii, 384.

Hickinbottom, *Wilfrid John.* See *Joseph* **Reilly.**

Hiege, *C.* See *Richard* **Zsigmondy.**

Higgins, *Harold Leonard*, effect of alcohol on the respiration and the gaseous metabolism in man, A., i, 489.

Higgins, *Harold Leonard*, and *Williams McKim* **Marriott**, a colorimetric method for the estimation of the percentage of carbon dioxide in the air, A., ii, 270.

Hildebrand, *Joel H.* See *Donald B.* **Keyes.**

Hilgendorff, *Gustav.* See *Emil* **Erlenmeyer.**

Hill, *Arthur E.*, inconstancy of the solubility product. II., A., ii, 242.

Hill, *J. Bennett*, new derivatives of tungsten, A., ii, 36.

Hiller, *Alma*, identification of the pentose in a case of pentosuria, A., i, 497.
  estimation of small amounts of sugar in the urine, A., ii, 394.

Hiller, *Alma*, and *Herman O.* **Mosenthal**, relation between the water and the dextrose concentration of the blood, A., i, 99.

Hilliger, *E.* See *Karl von* **Auwers.**

Hinck, *Claus Friedrich.* See *Max* **Trautz.**

Hindmarsh, (*Miss*) *Ellen Margaret*, (*Miss*) *Isabel* **Knight**, and *Robert* **Robinson**, 5-bromoguaiacol and some derivatives, T., 940, A., i, 693.

Hine, *Thomas B.*, electrical conductivities of dilute sodium, potassium, and lithium amalgams, A., ii, 287.

Hines, *H. M.* See *Louis* **Baumann.**

Hinsberg, *Oscar* [*Heinrich Daniel*], diaryldisulphones, A., i, 135.

the reaction between aromatic sulphinic acids and di- and tri-phenylcarbinols, A., i, 328.

dihydroxydiarylsulphones, A., i, 575.

valency centres, A., ii, 173, 461.

Hintikka, *S. V.* See *Gustav* **Komppa.**

Hirsch, *Julius*, the oxidation of alcohol by the liver of animals which have acquired tolerance and of those which have not, A., i, 67.

Hirst, *C. T.* See *Joseph Eames* **Greaves.**

Hirzel, *H.* See *Hermann* **Staudinger.**

Hissink, *David Jacobus*, action of various salt solutions on the permeability of the soil, A., i, 509.

Hitchcock, *E. B.* See *Percy Edgar* **Brown.**

Hoagland, *D. R.*, the effect of hydrogen and hydroxyl-ion concentration on the growth of barley seedlings, A., i, 619.

Hoagland, *Ralph*, estimation of dextrose in muscular tissue, A., ii, 515.

Hoagland, *Ralph*, and *C. M.* **Mansfield,** glycolytic properties of muscular tissue, A., i, 674.

function of muscular tissue in urea formation, A., i, 674.

Hodes, *F.*, the estimation of hydroxy-fatty acids, A., ii, 429.

Höber, *V. Rudolf*, narcosis, A., i, 68.

Hoeflake, (*Mlle.*) *J. M. A.* See *Arnold Frederik* **Holleman.**

Hörner, *Friedrich*, staurolite, A., ii, 325.

Hörner, *Friedrich.* See also *Ernst Anton* **Wülfing.**

Hoesch, *Kurt*, and *Thadäus von* **Zarzecki,** a new synthesis of aromatic ketones. II. Artificial production of maclurin and related ketones, A., i, 342.

Hofe, *Carl von.* See *Theodor* **Curtius.**

Hoff, (*Mlle.*) *Agnes.* See *Einar* **Biilmann.**

Hoffmann, *Josef*, water content of crystalline sodium tetraborate, A., ii, 206.

Hofman, *H. O.*, and *W.* **Wanjukow,** the decomposition of metallic sulphates by heat, A., ii, 465.

Hofmann, *Alice.* See *Hans* **Meyer.**

Hofmann, *Karl Andreas*, and *Ralf* **Ebert,** catalysis of hydrogen and oxygen mixtures at the ordinary temperature by moistened contact substances, A., ii, 25.

Hogan, *Albert G.*, maize as a source of protein and ash for growing animals, A., i, 363.

effect of high temperatures on the nutritive value of foods, A., i, 492.

Holding, *W. A.* See *W. H.* **MacIntire.**

Holgen, *H. J.*, Chinese alchemy, A., ii, 305.

history of Chinese mineralogy and chemical technology, A., ii, 326.

the period of the alchemists Isaac of Holland and Jan Isaac of Holland, A., ii, 461.

Holland, *E. B.*, *J. C.* **Reed,** and *J. B.* **Buckley,** *jun.*, estimation of stearic acid in butter fat, A., ii, 50.

Holland, *W. W.* See *Joseph Christie Whitney* **Frazer.**

Hollande, *A. Ch.*, and *L.* **Thévenon,** palpitation and caffeine; detection of caffeine in urine, A., ii, 55.

Hollatz, *E.* See *Erwin* **Rupp.**

Holleman, *Arnold Frederik*, the preparation of the six dichlorophenols and some of their properties, A., i, 556.

Holleman, *Arnold Frederik*, and (*Mlle.*) *J. M. A.* **Hoeflake,** nitration of *p*-tolyl carbonate, A., i, 133.

Hollins, *C.*, application of the Gutzeit test to works estimation of arsenic, A., ii, 382.

Holmberg, *Bror*, stereochemical studies. II. Action of potassium xanthate on salts of the halogeno-succinic acids, A., i, 115.

Holst, *G.*, and *E.* **Oosterhuis,** the melting-point of palladium and Wien's constant C_2, A., ii, 144.

Holtz, *Johanna.* See *Wilhelm* **Schlenk.**

Holz, *Wilhelm.* See *Julius* **Bredt.**

Homberger, *Alfred W.*, and *C. S.* **Marvel,** rate of turbidity in beverages containing maltose, dextrose, or maltose and dextrose, A., i, 370.

Homer, (*Miss*) *Annie*, reaction of sera as a factor in the successful concentration of anti-toxic sera by the methods at present in use, A., i, 497.

Honda, *Kôtarô*, and *Takejirô* **Murakami,** structure of magnet steel and its change with heat treatment, A., ii, 535.

Hooker, *Marian O.* See *Martin Henry* **Fischer.**

Hoover, *D. H.* See *John James Rickard* **Macleod.**

Hopkins, *B. Smith*, and *Clarence William* **Balke,** purification and atomic weight of yttrium, A., ii, 34.

Hopkins, *Cyril George*, soil bacteria and phosphates, A., i, 431.

Hopkins, *Frederick Gowland.* See *Harold* **Ackroyd.**

Hordh, *Ulaus.* See *Luis* **Guglialmelli.**

Horiba, *Shinkichi*, studies of solution. I. The change of molecular solution volumes in solutions, A., ii, 409.

studies of solution. II. A conception of osmotic pressure, A., ii, 410.

Horváth, *Béla von*, chemical constitution of bauxite from Bihar, Hungary, A., ii, 487.

Hoschek, *Arthur Baron*, condensation of indoles with aromatic aldehydes, A., i, 167.

Hoschek, *Arthur Baron*. See also *Oskar* **Baudisch.**

Houben, *Josef*, and *Alexander* **Pfau**, catalytic hydrogenation of hydroxy- and amino-benzoic acids, A., i, 25.
[*iso*nortropinone], A., i, 162.

Howard, *Bernard Farmborough*, and *O.* **Chick**, decomposition of quinine hydrogen sulphate, A., i, 581.

Howard, *David*, obituary notice of, T., 342.

Howden, *R.*, analysis of white metal alloys; estimation of lead, copper, and antimony, A., ii, 580.

Howell, *Janet T.* See *Gladys A.* **Anslow.**

Howell, *William Henry*, structure of the fibrin-gel and theories of gel-formation, A., i, 101.

Howland, *John*, and *Williams McKim* **Marriott**, acid-base equilibrium in the body, A., i, 366.

Hoyt, *Samuel L.* See *Arvid E.* **Nissen.**

Hradecky, *Karl*, the action of selenic acid on osmium, A., ii, 483.

Hubaleck, *Max.* See *Carl* **Paal.**

Hubbard, *Roger S.*, titration method for estimating minute quantities of acetone, A., ii, 279.

Hudson, *Claude S.*, a relation between the chemical constitution and the optical rotatory power of the phenylhydrazides of certain acids of the sugar group, A., i, 318.

Hudson, *Claude S.*, and *J. K.* **Dale**, the forms of *d*-glucose and their mutarotation, A., i, 320.

Hudson, *Claude S.*, and *T. S.* **Harding**, the preparation of xylose, A., i, 444.

Hudsen, *Claude S.*, and *James McIntosh* **Johnson**, the rotatory powers of some new derivatives of gentiobiose, A., i, 446.

Hudson, *Claude S.*, and *H. L.* **Sawyer**, the preparation of pure crystalline mannose and a study of its mutarotation, A., i, 321.

Hudson, *Claude S.*, and *E.* **Yanovsky**, indirect measurements of the rotatory powers of some α- and β-forms of the sugars by means of solubility experiments, A., i, 445.

Hudson, *Claude S.* See also *Frederick Burr* **La Forge.**

Hüttlinger, *A.* See *Alexander* **Gutbier.**

Hüttner, *Karl.* See *Franz* **Mylius.**

Hulbert, *E. O.*, and *J. F.* **Hutchinson**, the light absorption of an aqueous solution of sodium sulphate, A., ii, 557.

Hulbert, *E. O.*, *J. F.* **Hutchinson**, and *Harry Clary* **Jones**, absorption-coefficient of solutions of cobalt chloride in water and various alcohols for monochromatic radiation, A., ii, 161.

Hulett, *George Augustus.* See *W. M.* **Bovard**, *J. H.* **Capps**, and *Frank M.* **Seibert.**

Hull, *Mary.* See *John Harper* **Long.**

Hulton, *Henry Francis Everard.* See *Julian Levett* **Baker.**

Humphrey, *C. J.* See *Ernest J.* **Pieper.**

Humphrey, *George Colvin.* See *Edwin Bret* **Hart.**

Humphrey, *Irwin W.*, nitration of toluene to trinitrotoluene, A., i, 18.

Humphrey, *Irwin W.* See also *Benjamin T.* **Brooks.**

Hunter, *Andrew*, comparative biochemistry of purine metabolism. III. The presence of allantoin in mammalian blood, A., i, 184.

Hunter, *Andrew*, and *W. R.* **Campbell**, a hitherto neglected factor affecting the estimation of minute quantities of creatinine, A., ii, 110.

Hurtley, *William Holdsworth.* See *Edward* **Cahen.**

Huston, *Ralph C.*, and *Theodore E.* **Friedemann**, action of aromatic alcohols on aromatic compounds in the presence of aluminium chloride. I., A., i, 19.

Hutchinson, *J. F.* See *E. O.* **Hulbert.**

Hutin, *G.*, automatic estimation of carbon dioxide (carbonates) in soils; classification of soils, A., ii, 541.

Hynd, *Alexander.* See *Charles* **Crowther.**

I.

Illingworth, *C. B.* See *George Leslie* **Kelley.**

Imhof, *A.*, triboluminescence, A., ii, 229.

Incze, *Georg*, yellow mercuric oxide as a standard in alkalimetry, A., ii, 327.
estimation of hydrogen sulphide in water at the place where the sample is collected, A., ii, 502.

Irmann, *Roland*, studies in alloys resistant to sulphuric acid by improvement of the resistance of nickel, A., ii, 478.

Irvine, *James Colquhoun*, and *George* **Robertson**, evidence indicating the existence of a new variety of fructose; a reactive form of methylfructoside, A., i, 79.

Isaac, *Salo,* intermediate metabolism in experimental phosphorus poisoning, A., i, 678.

Isaac, *Salo,* and *A.* **Loeb,** respiratory metabolism of the artificially perfused livers from dogs after phosphorus poisoning, A., i, 678.

Isaac, *Salo.* See also *Gustav* **Embden.**

Ishikawa, *Fusao.* See *Mitsuru* **Kuhara.**

Ito, *Hiizu,* estimation of hippuric acid in urine, blood, muscles, and liver, A., ii, 52.

Ivanov, *A. A.* See *Sergius V.* **Lebedev.**

Ivanov, *L. L.,* the Brahin meteorites, A., ii, 498.

Ivanov, *V. N.,* new method of precipitation of platinum sulphide, and analysis of platinised asbestos, A., ii, 154.

Izmailski, *V. A.,* determination of the free alkali hydroxide in soap, A., ii, 153.

J.

Jacobs, *W.,* the system H_2O-Bi_2O_3-HCl at 30°, A., ii, 176.

Jacobs, *Walter Abraham,* and *Michael* **Heidelberger,** preparation of β-chloro- and β-bromo-propionic acids, A., i, 534.

methods for the acylation of aromatic amino-compounds and carbamides, with especial reference to chloroacetylation, A., i, 552.

the ferrous sulphate and ammonia method for the reduction of nitro- to amino-compounds, A., i, 559.

unsymmetrical derivatives of aromatic diamines, A., i, 583.

nitro- and amino-phenoxyacetic acids, A., i, 695.

Jacoby, *Martin,* general conceptions of intoxication. III. The stimulative action of lecithin on ferment formation, A., i, 71.

general conceptions of intoxication. IV. The nature of substances which accelerate the formation of ferments, A., i, 106.

general conceptions of intoxication. V. The stimulative action of dextrose on the formation of ferments, A., i, 106.

the formation of ferments, A., i, 305, 430, 528.

general conceptions of intoxication. II. Protection against "structure" poisons; a method for biochemical detection of small amounts of substances, A., ii, 54.

Jaeger, *Frans Maurits,* the temperature-coefficients of the free molecular surface energy of liquids between − 80° and 1650°. XVII. The relations between the molecular cohesion of liquids at their melting- and boiling-points and their absolute melting- and boiling-temperatures respectively, A., ii, 71.

Jaeger, *Frans Maurits,* and *Jul.* **Kahn,** the temperature-coefficient of the free molecular surface energy of liquids between −80° and 1650°. XV. The determination of the specific gravity of molten salts and of the temperature-coefficient of their molecular surface energy, A., ii, 69.

the temperature-coefficients of the free molecular surface energy of liquids between −80° and 1650°. XVI. The surface tension of some halogen compounds of sulphur, phosphorus, arsenic, antimony, and bismuth, A., ii, 70.

Jänecke, *Ernst,* transition of Na_2SO_4, A., ii, 15.

the separation and thermal metamorphosis of the Zechstein salts according to the hypothesis of Rózsa, A., ii, 265.

a complete review of solutions of oceanic salts. I. and II., A., ii, 527.

Jaffé, *Dora.* See *Wilhelm* **Steinkopf.**

James, *Charles.* See *A. J.* **Grant.**

Jamieson, *George Samuel,* the double salts of cæsium chloride with calcium and strontium chlorides, A., ii, 139.

the estimation of molybdenum by potassium iodate, A., ii, 275.

new method for the estimation of hydrogen peroxide, A., ii, 500.

Jansen, *Barend Cœnraad Petrus,* transformation of arginine into creatine in the animal organism, A., i, 606.

method for accurately estimating arginine in proteins, A., ii, 184.

Jansen, *J. D.,* nitro-derivatives of alkyltoluidines and the relation between their molecular refractions and those of similar compounds, A., i, 128.

the distinction between methylated nitroanilines and their nitrosoamines by means of refractometric determinations, A., ii, 401.

Jayson, *Alfred R.,* and *Ralph E.* **Oesper,** influence of added substances on the end-point in the iodometric titration of hydrogen sulphide, A., ii, 577.

Jean, the influence of extracts of the genital glands on phosphorus metabolism, A., i, 304.

Jellinek, *Ernst*. See *Otto* **Ruff.**

Jellinek, *Karl*, the osmotic–kinetic theory of dilute solutions, A., ii, 294.

Jensen, *H. R.*, estimation of strychnine in *Nux vomica*, A., ii, 56.

Jeutter, *Adolph*. See *Hugo* **Kauffmann.**

Ježek, *B.*, and *Ant.* **Simek**, crystallised ferric orthoarsenate, A., ii, 491.

Jilek, *A*. See *František* **Slavík.**

Joachimoglu, *Georg*, comparison of the actions of *d*-, *l*-, and *i*-camphor. I. Toxicity to cats. II. Action on the frog's heart. III. Antiseptic action, A., i, 528.

the estimation of the adsorption capacity of animal charcoal, A., ii, 42.

Joachimoglu, *Georg*. See also *E.* **Friedberger.**

Joachimowitz, *Marianne*, a new reagent for phloroglucinol and catechol; the distribution of these substances in the plant kingdom, A., i, 682.

Jörgensen, *Ingvar*, and *Franklin* **Kidd**, some photochemical experiments with pure chlorophyll and their bearing on theories of carbon assimilation, A., i, 74.

Jörgensen, *Ingvar*. See also *Walter* **Stiles.**

Jörlander, *Henrik*, anisoylphenylethylene oxide, A., i, 222.

anisoylphenylethylene oxide and other keto-oxido-compounds, A., i, 343.

Johannessohn, *Fritz*, the content in suprarenin [adrenaline] in the ordinary commercial preparations and the methods of estimation, A., ii, 55.

Johlin, *Jacob Martin*, diphenylbutadiene, A., i, 329.

Johns, *Carl Oscar*, and *Joseph F.* **Brewster**, kafirin, an alcohol-soluble protein from kafir, *Andropogon sorghum*, A., i, 108.

Johns, *Carl Oscar*, and *David Breese* **Jones**, proteins of the peanut, *Arachis hypogaea*. I. The globulins arachin and conarachin, A., i, 191.

proteins of the peanut, *Arachis hypogaea*. II. Distribution of the basic nitrogen in the globulins arachin and conarachin, A., i, 505.

Johns, *Carl Oscar*. See also *Lewis H.* **Chernoff**, and *David Breese* **Jones.**

Johnsen, *Arrien*, the probable movement of atoms in bismuth during crystal gliding, A., ii, 143.

Johnson, *Alfred J.* See *Joseph Howard* **Mathews.**

Johnson, *James McIntosh*, and *Solomon Farley* **Acree**, the rearrangement of 3-allyloxy-1-phenyl-4-methylurazole, A., i, 480.

Johnson, *James McIntosh*. See also *Claude S.* **Hudson.**

Johnson, *Treat Baldwin*, and *George C.* **Bailey**, amines. V. The structure of vitiatine; synthesis of methylethylenediamine, A., i, 9.

Johnson, *Treat Baldwin*, and *Sidney E.* **Hadley**, pyrimidines. LXXXIV. Transformation by hydrolysis of secondary pyrimidine nucleosides into iminazole combinations, A., i, 585.

pyrimidines. LXXXV. Synthesis of a secondary nucleoside of thymine and its conversion into a derivative of glyoxaline by hydrolysis with acids, A., i, 667.

Johnson, *Treat Baldwin*, and *Dorothy A.* **Hahn**, hydantoins. XXXIX. Synthesis of the polypeptide-hydantoin; tyrosylglycine-hydantoin, A., i, 475.

Johnston, *John*, and *E. D.* **Williamson**, the rôle of inorganic agencies in the deposition of calcium carbonate, A., ii, 213.

Jona, *Temistocle*, fenchone in cryoscopy, A., ii, 524.

Jones, *David Breese*, and *Carl Oscar* **Johns**, proteins from the jack bean, *Canavalia ensiformis*, A., i, 191.

Jones, *David Breese*. See also *Carl Oscar* **Johns.**

Jones, *David Trevor*, the thermal decomposition of low temperature coal tar, A., i, 193.

Jones, *Francis*, action of hydrogen on sulphuric acid, A., ii, 530.

Jones, *F. B.* See *Percy E.* **Spielmann.**

Jones, *Harry Clary*. See *E. O.* **Hulbert.**

Jones, *Lauder William*, and *Leonora* **Neuffer**, the preparation of alkyloxyurea [alkyloxyaminoformyl] chlorides and their relation to esters of carbon dioxide oxime, RO·N:C:O, A., i, 325.

hydroxamic acids related to *α*-hydroxy-acids and to acrylic acid, and a study of their rearrangements, A., i, 325.

Jones, *Lauder William*, and *M. Cannon* **Sneed**, dichloroacethydroxamic acid and its rearrangement, and aminoacethydroxamic acid, A., i, 326.

β-benzylformhydroxamic acid, A., i, 330.

Jones, *Lauder William*, and *Louis F.* **Werner**, aliphatic hydroxylammonium salts and hydroxamic acids with halogen substituents, A., i, 380.

Jones, *Samuel Mansfield*, and *Walter* **Spaans**, volumetric estimation of indigotin, A., ii, 56.

Jones, *Thomas Gilbert Henry*, and *Robert* **Robinson**, experiments on the orientation of substituted catechol ethers, T., 903 ; A., i, 69.

Jones, *Walter*, and *B. E.* **Read**, adenine–uracil–dinucleotide and the structure of yeast–nucleic acid, A., i, 232.

  mode of nucleotide linking in yeast–nucleic acid, A., i, 233.

  uracil–cytosine–dinucleotide, A., i, 596.

  structure of the purine mononucleotides, A., i, 597.

Jonge, (*Mlle.*) *J. A. de*, activation of pancreatic lipase by cholates, A., i, 362.

Jorissen, *Willem Paulinus*, Isaac of Holland and Jan Isaac of Holland, A., ii, 198, 529.

Joscht, *A.* See *Tadeusz* **Chrzaszcz.**

Joseph, *Alfred Francis*, and *William Norman* **Rae**, chromium phosphate, T., 196 ; A., ii, 210.

Jowleff, *W.* See *Paul* **Pfeiffer.**

Judd, (*Miss*) *Hilda Mary*, and *G. A. R.* **Kon**, preparation of 2:6-dimethylpiperidines substituted in the 2 position, including their 1-methyl derivatives, A., i, 282.

Jurkowski, *S.* See *Otto* **Kym.**

Justin-Mueller, *Ed.*, estimation of total nitrogen ; accurate method of estimating ammonia volumetrically after destruction of organic matter in the presence of mercury, A., ii, 39.

  indoxyl in urine, A., ii, 57.

  simplified preparation of the reagent with phenolphthalein for the detection of blood in urines, A., ii, 432.

  the detection of cryogenine in urines, A., ii, 518.

  rapid volumetric and clinical estimation of albumin, A., ii, 555.

K.

Kafuku, *K.*, volatile constituents of leaves of *Alpina nutans*, Roscoe, A., i, 576.

Kahn, *Jul.* See *Frans Maurits* **Jaeger.**

Kahn, *R. L.*, Folin and Denis's method for the estimation of nitrogen by direct nesslerisation, and its application to spinal fluids, A., ii, 100.

Kaiser, *O.* See *Amé* **Pictet.**

Kallenberg, *Sten*, stereochemistry of rhodanines. I., A., i, 279.

Kallós, *Josef*, simple new reaction for bile pigments, A., ii, 555.

Kamm, *Oliver*, *Harry Bruce* **McClugage**, and *A. W.* **Landstrom**, syntheses in the naphthalene series, A., i, 455.

Kamm, *Oliver.* See also *Clarence G.* **Derick**, and *Moses* **Gomberg.**

Kanhäuser, *Franz.* See *Hugo* **Ditz.**

Kanov, *F. P.* See *Nicolai S.* **Kurnakov.**

Kaplanova, *L.*, crystallography of some compounds of glutamic acid and glutiminic acid, A., i, 547.

Karaoglanow, *Z.*, detection of calcium in the presence of barium and strontium, A., ii, 333.

  properties of barium sulphate, A., ii, 387.

Karmanov, *S. G.* See *Vladimir Vasilevitsch* **Tschelincev.**

Karr, *Walter G.* See *Howard B.* **Lewis**, and *C. G.* **MacArthur.**

Karrer, *P.*, chelerythrine, A., i, 349.

  tetramethyldiaminophenazine, A., i, 356.

  the alkaloids of ipecacuanha. II., A., i, 409.

  some new compounds of dextrose, A., i, 539.

Karzeff, *Nikolaus.* See *Oskar* **Baudisch.**

Kassner, *Georg*, polysilicates and polyplumbates, A., ii, 314.

Kastle, *Joseph Hoeing*, and *G. Davis* **Buckner**, evidence of the action of oxydases within the growing plant, A., i, 372.

Katayama, *Massao*, preparation of phenyl-*a*-naphthylamine, A., i, 645.

Katz, *Johan Rudolf*, the laws of swelling. I. The swelling in water without complications, A., ii, 245.

Kauffmann, *Hugo*, *K.* **Burr**, *Adolph* **Jeutter**, and *Emil* **Meyer**, the state of saturation of chromophores, A., i, 391.

Kauffmann, *Hugo*, [with *Adolph* **Jeutter**, and *Emil* **Meyer**], chromophores with auxochromic functions, A., i, 394.

Kaufmann, *Adolf*, the cinchona alkaloids, A., i, 471.

Kaufmann, *Adolf*, and *Paul* **Haensler**, quinaketones, A., i, 472.

Kaufmann, *Adolf*, and *Victor Petheou de* **Petherd**, nitration of quinolone and carbostyril ethers, A., i, 354.

Kaufmann, *Adolf*, *Ernst* **Rothlin**, and *Paul* **Brunnschweiler**, degradation of the cinchona alkaloids. I., A., i, 50.

Kaufmann, *Wilhelm von*, reaction between starch and formaldehyde, and the supposed diastatic properties of formaldehyde, A., i, 251.

Kayser, *E.*, the apiculate yeasts, A., i, 432.

Keane, *L. A.*, plaster of Paris, A., ii, 89.

Keegan, *H. B.* See *Ebenezer Henry* **Archibald.**

Kehrmann, *Friedrich*, and *G.* **Falconnier**, tetramethyldiaminophenazine, A., i, 356.

Kehrmann, *Friedrich*, and *Stanislas* **Hempel**, constitution and colour. V. The colour of azo-compounds and their salts. II., A., i, 593.

Kehrmann, *Friedrich*, and *Alexander* **Herzbaum**, monosulphonic acids of quinone-imide dyes, A., i, 591.

Kehrmann, *Friedrich*, [with *Adrien* **Robert**, and *Maurice* **Sandoz**], dyes of the methylene-blue group. III. Moderated action of aliphatic amines on phenazthionium salts, A., i, 226.

Kehrmann, *Friedrich*, [with *René* **Speitel**, *Max* **Weilenmann**, and *Wladislaus* **Poplawski**], azine dyes, A., i, 415.

Kehrmann, *Friedrich*, and *Knut* **Stahrfoss**, the so-called chromoisomerism of salts of phenylmethylacridinium, A., i, 221.

Keister, *J. T.*, application of the cryoscopic method for estimating added water in milk, A., ii, 550.

Kelber, *C.*, catalytic hydrogenation of organic compounds with base metals at the ordinary temperature; removal of halogens from organic halogen compounds, A., ii, 215.

Kelber, *C.* See also *E.* **Seel.**

Keller, *Oskar*, alkaloids of ipecacuanha root, *Uragoga ipecacuanha*. III., A., i, 409.

Kelley, *George Leslie*, a new tube for soda-lime; a new absorbent for carbon dioxide in steel analysis, A., ii, 43.

Kelley, *George Leslie*, *J. R.* **Adams**, and *J. A.* **Wiley**, apparatus for electrometric titration depending on the change of oxidation potential, and its application to the estimation of small quantities of chromium in steel, A., ii, 512.

Kelley, *George Leslie*, and *F. B.* **Myers**, analysis of alloys of nickel and zirconium, A., ii, 544.

Kelley, *George Leslie*, *F. B.* **Myers**, and *C. B.* **Illingworth**, estimation of tantalum in alloy steels, A., ii, 546.

Kelley, *Walter Pearson*, nitrification in semi-barren soils, A., i, 431.

Kellner, *Georg*, the binary systems of bromides of the alkalis and alkaline earths, A., ii, 469.

Kemble, *Edwin C.* See *James B.* **Brinsmade.**

Kemp, *A. R.* See *H. J.* **Lucas.**

Kempf, *Hubert*. See *Hartwig* **Franzen.**

Kempf, *Richard*, titration of iodine with thiosulphate, A., ii, 502.

Kendall, *E. C.*, active constituent of the thyroid; its isolation, chemical properties, and physiological action, i, 364.

Kendall, *James*, preparation of conductivity water, A., ii, 11.

water correction in conductivity determinations, A., ii, 234.

Kendall, *James*, and *Kenneth Potter* **Monroe**, the viscosity of liquids. II. The viscosity-composition curve for ideal liquid mixtures, A., ii, 524.

the viscosity of liquids. III. Ideal solutions of solids in liquids, A., ii, 525.

Kende, *Siegmund*, the action of soaps on the fermentative degradation of starch and glycogen, A., i, 615.

Kennaway, *Ernest Laurence*. See *Carl Hamilton* **Browning.**

Kennedy, *J. J.* See *William Ridgeley* **Orndorff.**

Kern, *J.* See *G.* **Hager.**

Kertész, *Zoltán*, volatile organic compounds, particularly ethereal oils, in the manufacture of sulphite cellulose, A., i, 8.

Kesseler, *Hans*. See *Georg* **Schroeter.**

Keyes, *Donald B.*, and *Joel H.* **Hildebrand**, the system aniline-hexane, A., ii, 565.

Keyes, *Frederick G.*, and *Henry A.* **Babcock**, thermo-dynamic contents of ammonia. I. The heat capacity of liquid ammonia, A., ii, 440.

Kichler, *A.* See *Josef* **Herzig.**

Kidd, *Franklin*. See *Ingvar* **Jörgensen.**

Kiliani, *Heinrich*, digitalis glucosides, A., i, 468.

Killian, *John A.* See *Victor Caryl* **Myers.**

Kiltinovic, *Stanislaw Stanislavovitsch*. See *Leo Alexandrovitsch* **Tschugaev.**

Kimball, *J. W.*, and *Ebenezer Emmet* **Reid**, esterification. VIII. The esterification of benzoic acid by isomeric butyl mercaptans, A., i, 88.

Kinder, *Hugo*, recovery of ammonium molybdate from the filtrates obtained in the estimation of phosphoric acid, A., ii, 321.

estimation of manganese in iron and steel according to the bismuth method, A., ii, 389.

iron oxide as standard in the volumetric estimation of iron in hydrochloric acid solution, A., ii, 391.

Kindler, *K.* See *Julius von* **Braun.**

Kindler, *Karl.* See *Paul* **Rabe.**

King, *Albert Theodore*, and *Frederick Alfred* **Mason**, manufacture of acetals, A., i, 5.

King, *Albert Theodore*, *Frederick Alfred* **Mason**, and *Samuel Barnett* **Schryver**, preparation of vinyldiacetoneamine [2:2:6-trimethyl-4-piperidone] and its salts, A., i, 95.

Kingsbury, *F. B.*, effect of bile and bile salts on the reaction between oleic acid and sodium hydrogen carbonate, A., i, 362.

Kingsbury, *F. B.*, and *J. P.* **Sedgwick**, uric acid content of the blood of newborn children, A., i, 601.

Kishida, *M.* See *Keisaku* **Shibata.**

Kjöllerfeldt, *Marcus*, permeability of cells. VII. Resorption of proteins and their degradation products from the peritoneal cavity of the rabbit, A., i, 605.

Klason, *Peter*, the normal content of arsenic in urine, A., i, 186.
  estimation of small quantities of arsenic, A., ii, 151.

Klaus, *Franz.* See *Oskar* **Baudisch.**

Klee, *Walter.* See *Johannes* **Gadamer.**

Klein, *Hermann.* See *Robert* **Kremann.**

Kliatchko, *J.*, and *Ch.* **Binggely**, electroreduction of the nitrates of potassium and lithium by the alternating current, A., ii, 355.

Kling, *André*, testing sulphuric acid used in the manufacture of dextrose [for arsenic], A., ii, 579.
  arsenical dextrose, A., ii, 579.

Klinger, *R.* See *E.* **Herzfeld.**

Klinkert, *J.* See *Paul* **Pfeiffer.**

Klooster, *H. S. van*, saturated solutions of potassium and magnesium sulphates, A., ii, 471.

Knack, *A. V.* See *Johann* **Feigl.**

Knecht, *Edmund*, estimation of nitrotoluenes, A., ii, 427.

Knight, *Cyril W.* See *Willet G.* **Miller.**

Knight, (*Miss*) *Isabel.* See (*Miss*) *Ellen Margaret* **Hindmarsh.**

Knop, *Josef.* See *Jaroslav* **Formánek.**

Knorr, *Angelo*, imino-esters. II. Mechanism of the formation of amidines, A., i, 255.
  imino-esters. III. The constitution of salts of the imino-esters, A., i, 547.

Knorr, *E. S.* See *L. G.* **Wesson.**

Knublauch, estimation of naphthalene [in coal gas] by picric acid, A., ii, 427.

Knudson, *Arthur.* See *W. R.* **Bloor.**

Knust, *Andreas*, and *Otto* **Mumm**, intramolecular rearrangement and ring closures with derivatives of benzoylacetamide, A., i, 414.

Kobayashi, *Matsusuke.* See *Gregory Paul* **Baxter**, and *Frank Austin* **Gooch.**

Kober, *Philip Adolph*, the efficiency of the aeration method for distilling ammonia; in answer to certain criticisms, A., ii, 40.
  improved nephelometer-colorimeter, A., ii, 266.
  pervaporation, perstillation, and percrystallisation, A., ii, 295.
  improvements in the copper method for estimating amino-acids, A., ii, 398.

Koch, *E. W.* See *A. L.* **Walters.**

Koch, *George P.*, effect of different salts on the formation of ammonia in soil, A., i, 622.

Koch, *P.*, estimation of chromium in ferrochrome, steel, and slags by the permanganate method, A., ii, 221.
  estimation of chromium in ferrochrome, A., ii, 337, 392.

Köhler, *Fritz*, the chromates of silver and the solid solutions with nitrates, A., ii, 32.

Koehler, *Z.* See *Julius von* **Braun.**

Koelsch, *F.*, toxicity of aromatic nitro-compounds, A., i, 716.

König, *E.* See *Otto* **Fischer.**

Koenig, *G. A.*, chemical and mineralogical observations, A., ii, 486.

Körner, *Wilhelm*, and *Angelo* **Contardi**, the sixth (η-) trinitrotoluene and the corresponding halogenated dinitro-substitution products, A., i, 85.

Körösy, *Kornél von*, sugar absorption and the pancreas, A., i, 714.

Kohler, *Elmer Peter*, and *James Bryant* **Conant**, the *cyclo*propane series. I. and II., A., i, 566, 568.

Kohn, *Moritz*, constitution of isatide, A., i, 175.

Kolls, *A. C.* See *H. C.* **Dollwig.**

Kolosovski, *N. A.*, formula for the calculation of the specific heat of aqueous-alcoholic solutions of different substances, A., ii, 65.
  [heat of solution in mixed solvents], A., ii, 67.

Kolthoff, *I. M.*, the alcohol test for milk, A., ii, 111.
  qualitative analysis of carbohydrate mixtures, A., ii, 223.
  titration of chlorides by Mohr's method, and its application to the examination of potable water, A., ii, 379.

Kolthoff, *I. M.*, estimation of the alkalinity and phosphoric acid content of the ash of feeding stuffs, A., ii, 386.
  argentometric estimation of bromides and iodides, A., ii, 420.
  titration of carbonic acid and its salts, A., ii, 506.
Kolthoff, *I. M.*, and *L. B. van* **Lohuizen**, [estimation of tin in tin-plate], A., ii, 426.
Kolthoff, *I. M.* See also *Hugo Rudolph* **Kruyt**, and *Nicolaas* **Schoorl**.
Komatsu, *Shigeru*, the stereochemistry of quinquevalent nitrogen. V. The betaines and the formation of unsaturated acids in plants. I., A., i, 139.
Komppa, *Gustav*, and *S. V.* **Hintikka**, synthesis of santene, A., i, 214.
Komppa, *Gustav*, and *R. H.* **Roschier**, nomenclature of the fenchenes; new method of preparing β-fenchene, A., i, 398.
  complete synthesis of a fenchene, A., i, 466.
Kon, *G. A. R.* See (*Miss*) *Hilda Mary* **Judd**.
Koningh, *Leonard de*, obituary notice of, T., 348.
Koopman, *H.* See *Johann* **Feigl**.
Koopman, *W.* See *L.* **Hamburger**.
Korber, *Josef.* See *Jaroslav* **Formánek**.
Kornfeld, *Gertrud*, the phenomena of suspended transformation, A., ii, 129.
Korschun, *Georgi*, and *A.* **Gounder**, saponification of 2:5-dimethylfuran-3:4-dicarboxylic ester at 50°, A., i, 91.
  saponification of some pyrrolemonocarboxylic and pyrroledicarboxylic esters at a temperature of 98·3–98·7°, A., i, 95.
  saponification of some esters of pyrroledicarboxylic acid at 50°, A., ii, 25.
Korten, *Ernst*, improvement in the use of the Gooch crucible, A., ii, 326.
Kowalski, *Z.* See *St.* **Opolski**.
Kozicki, *Georg von*, and *St. von* **Pilat**, use of Shukov's apparatus for molecular weight determinations, A., ii, 123.
Koziorovski, *W.* See *Stanislaus Jozef* **Thugutt**.
Kräuter, *J.* See *Alexander* **Gutbier**.
Kräutle, *Nora.* See *Alexander* **Gutbier**.
Kramer, *B.*, *J.* **Marker**, and *John Raymond* **Murlin**, pancreatic diabetes in the dog. II. Is the dextrose retained when sodium carbonate is administered to depancreatised dogs deposited as glycogen? A., i, 69.
Kramer, *B.* See also *John Raymond* **Murlin**.
Kramer, *J. G.* See *Willey* **Denis**.
Kraus, *Charles August*, mercury vapour pumps for operating against high pressures, A., ii, 567.
Krause, *Erich.* See *Gerhard* **Grüttner**.
Krause, *Ellis L.* See *Joseph Howard* **Mathews**.
Krause, *H.*, preparation of nitromethane and homologues, A., i, 377.
Krauskopf, *Francis Craig*, and *George* **Ritter**, the colours produced by resorcinol in solutions of certain salts and the use of these colours as a means of detecting resorcinol in the presence of other phenols, A., ii, 48.
Krauss, *Robert B.*, electrolytic diazotisation of an aliphatic compound, A., i, 548.
  the use of large glass-stoppered containers in autoclaving, A., ii, 462.
Krauss, *Robert B.*, and *Edward* **Crede**, preparation of halogen derivatives of catechol, homocatechol, and pyrogallol methyl ethers and sulphonic acids, A., i, 557.
Kravcov, *V. A.* See *G. E.* **Timofeev**.
Krell, *A.* See *Alexander* **Gutbier**.
Kremann, *Robert*, heavy oil of wine, A., i, 314.
Kremann, *Robert*, and *Hermann* **Breymesser**, theory of the electrolytic formation of plumbic chloride, A., ii, 573.
Kremann, *Robert*, and *Hermann* **Klein**, kinetics of furfuraldehyde formation from pentoses (arabinose), A., ii, 251.
Kremann, *Robert*, *Rudolf* **Schadinger**, and *Richard* **Kropsch**, electrolytic deposition of alloys and their metallographic examination. VII. Experiments on the cathodic preparation of pyrophoric deposits from glycerol-water solutions of iron salts with additions of other salts, particularly cerous chloride, A., ii, 574.
Kremer, *J. H.*, adsorption of odoriferous and other substances by lipoids, A., i, 607.
Kroneberg, *P. M.*, condensation of amines with formaldehyde, A., i, 170.
Kronmann, *S.* See *Emil* **Baur**.
Kropf, *Alfred*, source of error in the analysis of generator gas, A., ii, 541.
Kropsch, *Richard.* See *Robert* **Kremann**.
Kruber, *Otto.* See *Julius von* **Braun**.
Krüger, *Friedrich*, dependence of transport numbers on the nature of the solvent, A., ii, 118.

Krüger, *Friedrich*, and *E.* **Taege**, influence of catalyst poisons on the photo-electric sensitiveness of platinum, A., ii, 119.

Krummacher, *Otto*, oxyhæmoglobin crystals from the blood of guinea-pigs, A., i, 303.

Krumreich, *H.*, determination of the transport number of the silver ion in 0·01 *N*-silver nitrate solution in mixtures of ethyl alcohol and water at 40°, A., ii, 118.

Kruyt, *Hugo Rudolph*, the equilibrium solid–liquid–gas in binary systems which present mixed crystals. IV., A., ii, 133.
  current potentials of electrolyte solutions. II., A., ii, 403.
  the additivity of the specific volume in sols, A., ii, 407.

Kruyt, *Hugo Rudolph*, and *Willem Dirk* **Helderman**, the equilibrium solid–liquid–gas in binary systems which present mixed crystals. III., A., ii, 81.

Kruyt, *Hugo Rudolph*, and *I. M.* **Kolthoff**, colour change and degree of dispersity of indicators, A., ii, 452.

Kruyt, *Hugo Rudolph*, and *Jac. van der* **Spek**, mechanism of the precipitation process, A., ii, 563.

Kudicke, *R.*, and *H.* **Sachs**, the action of cobra poison on lecithin, A., i, 70.

Kühl, *Hans*, the destruction of underground building work by moorland sulphur, A., i, 76.

Kuenen, *Johan Pieter*, and *A. L.* **Clark**, critical point, critical phenomena, and a few condensation constants of air, A., ii, 405.

Kueny, *R.* See *Otto A.* **Oesterle.**

Küster, *William*, bile pigments. X. Bilirubin-ammonia and modifications of bilirubin, A., i, 421.

Küster, *William*, and *Johannes* **Weller**, synthesis of hæmatic acid and the oxidation of hæmatin, A., i, 443.

Kuhara, *Mitsuru*, and *Fusao* **Ishikawa**, the Beckmann rearrangement. VII. The rearrangement of ethyl*syn*benzhydroximic acid, the different acid chlorides, and its benzenesulphonic ester, A., i, 87.

Kuhara, *Mitsuru*, and *Hikohei* **Watanabe**, the Beckmann rearrangement. VI. The rate of rearrangement of phenylmethylketoxime by different acid chlorides, the spontaneous rearrangement of its benzenesulphonic ester, and the synthesis of phenylacetaminobenzenesulphonate, A., i, 87.

Kunder, *Herm.* See *Max* **Busch.**

Kuriyama, *Shigenobu*, fate of alkali-blue in the organism, A., i, 70.

Kuriyama, *Shigenobu*, and *Lafayette Benedict* **Mendel**, physiological behaviour of raffinose, A., i, 611.

Kurnakov, *Nicolai S.*, and *N. N.* **Beketov**, viscosity of the system stannic chloride–ethyl propionate, A., ii. 361.

Kurnakov, *Nicolai S.*, *S. I.* **Perlmutter**, and *F. P.* **Kanov**, viscosity of binary systems containing stannic or antimony chloride, A., ii, 360.

Kursanov, *N. I.*, menthanecarboxylic acids, A., i, 137.
  composition of crude menthyl chloride, A., i, 151.
  dextro-rotatory menthyl iodide, A., i, 396.
  menthylphenols, A., i, 396.
  phenyl *cyclo*hexyl ether and its isomeration to *cyclo*hexylphenol, A., i, 398.

Kurtz, *Paul.* See *Wilhelm* **Wislicenus.**

Kuss, *Ernst.* See *Alfred* **Stock.**

Kutter, *Viktor*, the application of vortex rings in the determination of surface tensions, A., ii, 69.
  the periodic system of the elements and spectrum analysis, A., ii, 185.

Kym, *Otto*, and *S.* **Jurkowski**, some α-styrylbenziminazoles and their azo-dye derivatives, A., i, 175.

Kyropoulos, *S.*, differentiation of the internal structure of different species of silica by their Röntgen ray interference patterns, A., ii, 468.

Kyropoulos, *S.* See also *L.* **Hahn.**

L.

Laage, *E.* See *Richard* **Stoermer.**

Laan, *Bernhard van der.* See *Theodor* **Curtius.**

Laar, *Johannes Jacobus van*, the fundamental values of the quantities b and $\sqrt{a}$ for different elements in connexion with the periodic system. III. Discussion of the different groups of elements separately, A., ii, 67.
  the fundamental values of the quantities b and $\sqrt{a}$ for different elements in connexion with the periodic system. IV. The elements of the halogen, oxygen, and nitrogen groups, A., ii, 67.

Laborde, *J.* [*B. Vincent*], the reactions of the white turbidity of wines, A., i, 373.
  the aldehydes of wines, A., i, 532.

Labouchère, *A.* See *Amé* **Pictet.**

Laer, *Marc van,* electrolytic migration; electrolysis of solutions of mixed alkaline salts, A., ii, 404.

La Forge, *Frederick Burr,* *d*-mannoketoheptose, a new sugar from the avocado, A., i, 118.

La Forge, *Frederick Burr,* and *Claude S.* **Hudson,** sedoheptose, a new sugar from *Sedum spectabile.* I., A., i, 444.

Lagers, *G. H. G.,* estimation of total nitrogen, A., ii, 329.

Lajoux, *Henri,* estimation of mercury in basic mercuric salicylate and its isomerides, A., ii, 273.

Lajoux, *Henri,* and *L.* **Ronnet,** table for the analysis of foods containing sugar, A., ii, 582.

Lakhumalani, *Jamiat Vishindas.* See *John Joseph* **Sudborough.**

Lakon, *Georg,* the protein content of variegated leaves investigated by Molisch's macroscopic method, A., i, 504.

Lamb, *A. R.,* the Duclaux method for volatile fatty acids, A., ii, 277.

Lamb, *A. R.* See also *Arthur Wayland* **Dox.**

Lamble, *Alfred.* See *Robert Owen* **Griffith.**

Langdon, *Seth C.,* occurrence of free carbon monoxide in kelp (*Nereocystis luetkeana*), A., i, 372.

Landstrom, *A. W.* See *Oliver* **Kamm.**

Lange, *G.* See *Julius* **Tröger.**

Langmuir, *Irving,* constitution and fundamental properties of solids and liquids. I. Solids, A., ii, 19.
  constitution and fundamental properties of solids and liquids. II. Liquids, A., ii, 525.

Langreck, *F. B.* See *Le Roy* **McMaster.**

Lankshear, *Frederick Russell,* quantitative absorption spectra. II. A new ultra-violet photometer, A., ii, 283.

Lapworth, *Arthur,* (*Mrs.*) *Leonore Kletz* **Pearson,** and *Frank Albert* **Royle,** the pungent principle of ginger. I. The chemical characters and decomposition products of Thresh's "gingerol," T., 777; A., i, 571.

Lapworth, *Arthur,* and *Frederick Henry* **Wykes,** the pungent principle of ginger. II. Synthetic preparations of zingerone, methylzingerone, and some related acids, T., 790; A., i, 572.

Laquer, *Fritz.* See *Gustav* **Embden.**

Larsen, *Esper Signius,* eakleite, a new mineral from California, A., ii, 417.

Larsen, *Esper Signius,* and *George* **Steiger,** mineralogical notes, A., ii, 148.

Larsen, *Esper Signius,* and *Edgar Theodore* **Wherry,** halloysite from Colorado, A., ii, 265.
  leverrierite from Colorado, A., ii, 324.

Larsen, *Esper Signius.* See also *Roger Clark* **Wells.**

Larsen, *Louis M.* See *Jean* **Piccard.**

Laschtschenko, *P. N., S. F.* **Bykov,** and *S. V.* **Efremov,** thermoelectric properties of certain polymorphous metals, A., ii, 114.

Laske, *Karl.* See *Johannes* **Gadamer.**

Lathrop, *Elbert C.,* simple device for the automatic and intermittent washing of precipitates, A., ii, 367.

Latshaw, *W. L.,* comparison of methods for estimating nitrogen in soils, A., ii, 100.

Laudat, *M.,* estimation of chlorine in blood serum and other body fluids, A., ii, 539.

Laue, *M. von,* crystallography and Röntgen rays, A., ii, 166.

Launoy, *L.,* the sensitiveness of the general method of extraction of alkaloids in water, A., ii, 553.

Laurent, *Adrien.* See *Theodor* **Curtius.**

Lauschke, *Georg.* See *Otto* **Ruff.**

Law, *James.* See *Walter Norman* **Haworth.**

Leary, *J. T.,* and *S. H.* **Sheib,** influence of the coagulation by rennin on the gastric digestion of the proteins of milk, A., i, 184.
  the effect of the ingestion of aluminium on the growth of the young, A., i, 493.

Leavenworth, *Charles Samuel.* See *Thomas Burr* **Osborne.**

Le Bas, *Gervaise,* atomic volumes of oxygen and the halogens at the critical point, A., ii, 193.
  molecular refractivities of certain elements and simple compounds, A., ii, 349.
  the volumes of the atoms at absolute zero, A., ii, 357.
  influence of unsaturation on the molecular volumes of solid compounds, A., ii, 442.

Lebedev, *A.,* fermentation of dibasic acids. I. Malic acid, A., i, 188.

Lebedev, *Sergius V.,* and *A. A.* **Ivanov,** polymerisation of α-phenyl-$\Delta^{\alpha\gamma}$-butadiene, A., i, 126.

Le Chatelier, *Henri,* cristobalite, A., ii, 97.
  the synthesis of ammonia, A., ii, 257.
  the tempering of steel, A., ii, 477.

Le Chatelier, *Henri,* and *B.* **Bogitch,** the refractory properties of magnesia, A., ii, 573.

Le Chatelier, *Henri*, and *F.* **Bogitch**, the refractory properties of clay, A., ii, 319.

Le Chatelier, *Henri*, and *Eugene Louis* **Dupuy**, the heterogeneity of steels, A., ii, 535.

Lecoq, *Raoul*, the examination of oils used in soap-making, A., ii, 399.

Lederer, *Karl*, *o*- and *p*-triphenetyltelluronium salts, A., i, 134.
  o-phenetyltellurium compounds, A., i, 134.
  α-naphthyltellurium compounds, A., i, 134.
  p-phenetyltellurium compounds, A., i, 264.

Lederle, *P.* See *Felix* **Mach.**

Ledoux, *A.*, geometric properties of isomorphous mixtures; application to the rhombic and monoclinic pyroxenes, A., ii, 496.

Ledoux-Lebard, *R.*, and *A.* **Dauvillier**, the *L*-series of the elements of high atomic weights, A., ii, 283.

Leduc, [*Sylvestre*] *Anatole*, heats of vaporisation and maximum vapour pressures, A., ii, 193.
  dilatability of argon and neon; internal pressure in monatomic gases, A., ii, 356.

Lee, *Richard Edwin*, *Walter H.* **Fegely**, and *Frank H.* **Reichel**, phosphor-tin and a volumetric method for its analysis, A., ii, 427.

Léger, *Eugène*, the aloins, A., i, 276.
  the bromo-derivatives of aloe-emodin, A., i, 518.

Lehmann, *Franz*, estimation of arsenic. III. Application to iron arsenic pills, A., ii, 579.

Lehmann, *Franz*, and *G.* **Wolff**, methyl-red [as an indicator], A., ii, 326.

Leibbrandt, *F.* See *Kurt* **Hess.**

Leighton, *Alan*, new application of the Bunsen valve, A., ii, 28.

Leiningen, *Wilhelm* (*Graf*) *zu*, the absorption of organic dyes by colloidal soils, clays, etc., A., ii, 112.

Leitmeier, *Hans*, crystallised montmorillonite and a gel form of planerite, A., ii, 494.
  pisanite from Lading, Carinthia, A., ii, 537.

Lembert, *M.* See *Kasimir* **Fajans.**

Lemp, *J. F.*, and *H. G.* **Broderson**, estimation of halogens in organic compounds, A., ii, 539.

Lenher, *Victor*, and *M. P.* **Schultz**, recovery of molybdenum residues, A., ii, 416.

Lenk, *Emil*, modification of Fehling's method of sugar estimation, A., ii, 341.
  estimation of acetone substances in the urine, A., ii, 399.
  rapid method for the estimation of albumin and sugar in urine, A., ii, 555.

Lepetit, *Roberto*, action of alkalis and acids on sodium *p*-phenetidinomethanesulphonate. II., A., i, 198.
  certain products of the action of formaldehyde and a hydrogen sulphite on aromatic amines and their derivatives. I., A., i, 197.

Lepetit, *Roberto*, and *Carlo* **Maimeri**, groups of bases obtained from aromatic amines and formaldehyde, A., i, 452.

Le Roy, *Georges A.*, control of water supplies which have been chlorinated, A., ii, 98.
  method of rendering more sensitive colorimetric analyses, A., ii, 418.

Leschke, *Erich*, and *Ludwig* **Pincussohn**, ferments of human cerebrospinal fluid, A., i, 363.

Leuchs, *G. A.* See *Alexander* **Gutbier.**

Leuchs, *K.*, preparation of pure zirconium oxide free from iron, A., ii, 321.

Leulier, *A.*, explosive peroxide derivative of hexamethylenetetramine, A., i, 251.

Levene, *Phœbus A.*, the chemical individuality of tissue elements and its biological significance, A., i, 363.
  chondrosamine and its synthesis, A., i, 633.
  structure of yeast-nucleic acid, A., i, 670.

Levene, *Phœbus A.*, and *C. H.* **Allen**, oxidation of branched chain fatty acids. I. Action of hydrogen peroxide on the homologues of *iso*butyric acid, A., i, 3.

Levene, *Phœbus A.*, and *Gustave Morris* **Meyer**, relation between the configuration and rotation of epimeric monocarboxylic sugar acids. III. Phenylhydrazides, A., i, 631.
  cerebrosides. III. Conditions for hydrolysis of cerebrosides, A., i, 657.
  removal of nitric acid from solutions of organic compounds, A., ii, 530.

Levene, *Phœbus A.*, and *Clarence J.* **West**, the cerebrosides of brain tissue, A., i, 525.
  cerebrosides. IV. Kerasin, A., i, 657.
  cerebrosides. V. Cerebrosides of the kidney, liver, and egg yolk, A., i, 657.

Levi, *G.* See *Giuseppe* **Bruni.**

Lévy, *Meyer*. See *Paul* **Dutoit**.

Lewis, *Ernest Alfred*, obituary notice of, T., 348.

Lewis, *Gilbert Newton*, and *Thomas B.* **Brighton**, potential of the lead electrode, A., ii, 524.

Lewis, *Gilbert Newton*, and *Merle* **Randall**, free energy of bromine compounds, A., ii, 15.

Lewis, *Howard B.*, metabolism of sulphur. II. Influence of small amounts of cystine on the balance of nitrogen in dogs maintained on a low protein diet, A., i, 603.

Lewis, *Howard B.*, and *Walter G.* **Karr**, changes in the urea contents of blood and tissues of guinea-pigs maintained on an exclusive oat diet, A., i, 100.

Lewis, *Howard B.* See also *L. Millard* **Smith**.

Lewis, *Samuel Judd*, the ultra-violet absorption spectra of blood sera, A., ii, 62.

Lewis, *William Cudmore McCullagh*, studies in catalysis. VII. Heat of reaction, equilibrium constant, and allied quantities from the point of view of the radiation hypothesis, T., 457; A., ii, 302.

  studies in catalysis. VIII. Thermochemical data and the quantum theory; high temperature reactions, T., 1086.

  the effect of pressure on the equilibrium constant of a reaction in a dilute solution; a simple proof of the expression, A., ii, 456.

Lewis, *William Cudmore McCullagh*. See also *Robert Owen* **Griffith**.

Ley, *Heinrich*, the state of saturation of the unsaturated linking, A., i, 261.

Ley, *Heinrich*, and *K.* **Ficken**, internally complex salts. XV. Isomerism and absorption of light of internally complex salts, A., i, 706.

Liberi, *G.*, estimation of phosphorus in zinc phosphide, A., ii, 329.

Lichtenstein-Rosenblat, *S.* See *Isak* **Abelin**.

Lichtwitz, *Leopold*, autoregulation of the course of reaction in fermentative processes, A., i, 681.

Lidov, *Alexander Pavlovitsch*, oxidation of carbon by air at low temperatures in presence of iron and other metals, A., ii, 86.

  combination of carbon and nitrogen at the ordinary temperature, A., ii, 86.

  carbon dioxide from natural limestones, A., ii, 87.

Liebisch, *Theodor*, the course of crystallisation in ternary systems of chlorides of univalent and bivalent metals, A., ii, 248.

Liebner, *A.* See *Heinrich* **Schulze**.

Liesche, *Otto*. See *Ernst* **Beckmann**, and *Georg* **Schroeter**.

Liesegang, *Raphael Ed.*, malachite; formation of pseudomorphs, A., ii, 489.

Lifschitz, *Israel*, the state of saturation of chromophores, A., i, 558.

  the chromophore function, A., ii, 62, 435.

Lifschitz, *Israel*, and *Heinrich* **Lourié**, the indigo chromophore, A., i, 586.

Lilly & Co., *Eli*, combination of organic acids [salicylic acid and 2-phenylquinoline-4-carboxylic acid], A., i, 96.

  combination of organic acids [ester of 2-phenylquinoline-4-carboxylic acid and salicylic acid], A., i, 96.

  preparation of cephaeline allyl ether, A., i, 410.

Linden, *T. van der*, solubility of calcium sulphite in water and sugar solutions, A., ii, 311.

Lindet, *Léon* [*Gaston Aimé*], the phosphorus contained in animal proteins after their demineralisation, A., i, 60.

  the loss in alcoholic fermentation, A., i, 188.

Linhart, *George Augustus*, potential of the mercury electrode against the mercurous ion, A., ii, 13.

  applicability of the ferro-ferricyanide electrode to the measurement of the activities of electrolytes in concentrated solutions, A., ii, 233.

Linhart, *George Augustus*, and *Elliot Quincy* **Adams**, reduction of mercuric compounds, A., ii, 301.

Linz, *Armin*, comparative examination of the methods proposed for the estimation of the glycyrrhizin in liquorice root and in *Succus liquiritiæ*, A., ii, 430.

Lipman, *Charles Bernard*, and *P. S.* **Burgess**, ammonifiability versus nitrifiability as a test for the relative availability of nitrogenous fertilisers, A., i, 243.

Lippmann, *Edmund Oskar von*, occurrence of mellitic acid, A., i, 272.

Ljungdahl, *Malte*, the estimation of nitrogen in urine, A., ii, 578.

  the estimation of acetone, A., ii, 584.

Lloyd, *Percy Vivian*. See *Clarence Arthur* **Seyler**.

Lockemann, *Georg*, comparative investigations on the excretion of arsenic in human urine after injection of various arsenical medicaments, A., i, 495.

Loczka, *J.*, pyrargyrite from Nagybánya, Hungary, A., ii, 485.

Loeb, *A.* See *Salo* **Isaac**.

Loeb, *Jacques*, mechanism of the diffusion of electrolytes through the membranes of living cells. I. The necessity of a general salt effect on the membrane as a prerequisite for this diffusion, A., i, 66.
  mechanism of the diffusion of electrolytes through the membranes of living cells. II. Diffusion of potassium chloride out of the egg of *Fundulus* and the relative efficiency of different ions for the salt effect, A., i, 66.
  mechanism of the diffusion of electrolytes through the membranes of living cells. III. Analogy of the mechanism of the diffusion for acids and potassium salts, A., i, 67.
  mechanism of the diffusion of electrolytes through the membranes of living cells. IV. Ratio of the concentration required for the accelerating and antagonistic action on the diffusion of potassium salts, A., i, 102.
  similarity of the action of salts on the swelling of animal membranes and of powdered colloids, A., ii, 453.

Loeb, *Jacques*, and *John H.* **Northrop**, nutrition and evolution. II., A., i., 65.

Löffl, *K.*, estimation of glycerol, crude glycerol, and glycerol lyes, A., ii, 547.

Loevenhart, *Arthur Solomon.* See *H. C.* **Dollwig**.

Loew, [*Carl Benedict*] *Oscar*, nitrate assimilation, A., i, 615.

Loewe, *L.*, estimation of lævulose in presence of dextrose, A., ii, 49.

Loewy, *Adolf*, and *R.* **Wolffenstein**, the astringent action of aluminium salts, especially of the formate, A., i, 497.

Lohuizen, *L. B. van.* See *I. M.* **Kolthoff**.

Lomax, *Ernest Lawson*, *Albert Ernest* **Dunstan**, and *Ferdinand Bernard* **Thole**, pyrogenesis of hydrocarbons, A., i, 109.

Lombard, *Robert H.* See *Eugene Thomas* **Allen**.

Lombroso, *Ugo*, metabolism of dextrose in surviving organs. I. Action of intestinal tissue on dextrose circulating therein, A. i, 102.

Lombroso, *Ugo*, elements which condition the activity of glycolytic enzymes. I. The glycolytic enzymes of the pancreas, and blood corpuscles, A., i, 182.
  genesis of carbamide. I. Can muscular tissue generate carbamide? A., i, 493.

Lomholt, *Svend*, and *J. A.* **Christiansen**, estimation of small amounts of mercury in organic substances, A., ii, 424.

Long, *E. Tatum*, the formation of salt crystals from a hot saturated solution, A., ii, 243.

Long, *John Harper*, and *Frederic* **Fenger**, the normal reaction of the intestinal tract, A., i, 492.

Long, *John Harper*, and *Mary* **Hull**, the assumed destruction of trypsin by pepsin and acid. II. Observations on animals, A., i, 361.
  the optimum reaction in tryptic digestion. I., A., i, 485.
  the assumed destruction of trypsin by pepsin and acid. III. Observations on men, A., i, 602.

Loomis, *Albert G.*, and *Herman* **Schlundt**, concentration of radium in carnotite ores, A., ii, 31.

Loomis, *Nathaniel Edward*, and *Solomon Farley* **Acree**, effect of pressure on the potential of the hydrogen electrode, A., ii, 12.

Loomis, *Nathaniel Edward*, *J. L.* **Essex**, and *Merle R.* **Meacham**, applicability of the isohydric principle to decinormal mixtures of hydrochloric acid and potassium chloride, A., ii, 353.

Loomis, *Nathaniel Edward*, and *Merle R.* **Meacham**, tenth normal hydrochloric acid calomel electrode, A., ii, 13.

Loomis, *Nathaniel Edward*, *Chester Fewton* **Myers**, and *Solomon Farley* **Acree**, potential of the hydrogen electrode at different pressures, A., ii, 289.

López, *Eusebio*, estimation of sugars, A., ii, 514.

Lóránt, *A.* See *Hugo* **Rohonyi**.

Lorenz, *Richard*, and *I.* **Posen**, the theory of electrolytic ions. VIII. The mobility of some inorganic complex ions, A., ii, 14.
  the atomic theory. VIII. Space filling and mobility of complex inorganic ions, A., ii, 15.
  the theory of electrolytic ions. VII. Determination of the constitution of complex salts by mobility and conductivity, A., ii, 439.

Loring, *Frederick Henry*, diazomethane, A., i, 515.

Loughlin, *G. F.*, and *Waldemar Theodore* **Schaller**, crandallite, a new mineral, A., ii, 146.

Lourié, *Heinrich*. See *Israel* **Lifschitz.**

Lubrzynska, (*Miss*) *Eva*, the condensation of pyrrole-2-aldehyde with ketones, A., i, 52.

Lubs, *Herbert A.*, and *Solomon Farley* **Acree**, the sulphonephthalein series of indicators and the quinone-phenolate theory, A., ii, 97.

Lubs, *Herbert A.*, and *Solomon Farley* **Acree**, [with *Lawson* **Wilkins**], tautomerism; the tautomeric reactions of 1-phenyl-4:5-dihydro-1:2:4-triazole-5-one 3-methyl sulphone and its salts with diazomethane and with alkyl haloids, A., i, 479.

Lubs, *Herbert A.* See also *William Mansfield* **Clark.**

Lucas, *H. J.*, and *A. R.* **Kemp**, estimation of silver in organic compounds, A., ii, 542.

Luden, *Georgine*, cholesterol. III. Influence of bile derivatives in Bloor's method of estimation of cholesterol, A., ii, 275.

Ludwig, *Wilhelm*, measurements in the short-waved portion of the arc spectrum of vanadium, A., ii, 349.

Lüft, *K.* See *Th.* **Merl.**

Lungo, *Carlo del*, thermodynamic proof of Avogadro's law, A., ii, 68.

Lussana, *Silvio*, variation of the specific heat of gases with the pressure, A., ii, 120.

Lutz, *Louis*, and *G.* **Baume**, the toxicological and urological characterisation of 2:4-dinitrophenol, A., i, 611.

Lye, *O. G.* See *James Ernest* **Marsh.**

Lyman, *Henry*, calcium content of human blood, A., i, 491.

rapid method for estimating calcium in blood and milk, A., ii, 271.

Lyman, *J. A.*, and *Ebenezer Emmet* **Reid**, the identification of acids. II., A., i, 334.

Lyman, *John Franklin*, metabolism of fats. I. Utilisation of palmitic acid, glyceryl palmitate, and ethyl palmitate by the dog, A., i, 714.

metabolism of fats. II. Effect of feeding palmitic acid, glyceryl palmitate, and ethyl palmitate on the depôt fat in the white rat, A., i, 714.

Lyman, *John Franklin*, and *J. C.* **Trimby**, excretion of creatine and creatinine parenterally introduced, A., i, 240.

Lyons, *Edward*, and *Ebenezer Emmet* **Reid**, the identification of acids. III., A., i, 559.

M.

Mabery, *Charles Frederic*, the relations in composition of the different forms of natural bitumens, A., ii, 537.

MacArthur, *C. G.*, *F. G.* **Norbury**, and *Walter G.* **Karr**, the nitrogenous hydrolysis products of heart lecithin, A., i, 315.

Macbeth, *Alexander Killen*, and *Alfred Walter* **Stewart**, absorption spectra of substances containing conjugated and unconjugated systems of triple bonds, T., 829; A., ii, 522.

Macbeth, *Alexander Killen*. See also *Peter Joseph* **Brannigan.**

McBeth, *I. G.*, fixation of ammonia in soils, A., i, 511.

McBride, *Lois*. See *William Maurice* **Dehn.**

McBride, *Russel S.*, and *J. A.* **Scherrer**, reducing matter extractable from filter paper, A., ii, 326.

McCabe, *C. R.*, analysis of antimonial lead, A., ii, 333.

McCall, *Arthur G.*, physiological balance of nutrient solutions for plants in sand cultures, A., i, 75

McClendon, *J. F.*, composition, especially the hydrogen-ion concentration, of sea-water in relation to marine organisms, A., i, 105.

new buffer mixtures, standard tubes, and colorimeter for estimating the hydrogen-ion concentration of sea-water, A., ii, 266.

use of the van Slyke carbon dioxide apparatus for the estimation of total carbon dioxide in sea-water, A., ii, 423.

standardisation of a new colorimetric method for the estimation of the hydrogen-ion concentration, carbon dioxide tension, and carbon dioxide and oxygen content of sea-water, of animal heat, and of carbon dioxide of the air, with a summary of similar data on hydrogen carbonate solutions in general, A., ii, 423.

McClendon, *J. F.*, *A.* **Shedlov**, and *W.* **Thomson**, hydrogen-ion concentration of the contents of the ileum, A., i, 602.

tables for finding the alkaline reserve of blood serum, in health and in acidosis, from the total carbon dioxide or the alveolar carbon dioxide or the hydrogen-ion concentration at known carbon dioxide tension, A., i, 671.

McClugage, *Harry Bruce.* See *Oliver* **Kamm.**

McCollum, *Elmer Verner,* and *Walter* **Pitz,** vitamine hypothesis and deficiency diseases; experimental scurvy, A., i, 604.

McCollum, *Elmer Verner, Nina* **Simmonds,** and *Walter* **Pitz,** effects of feeding the proteins of the wheat kernel at different planes of intake, A., i, 184.
is lysine the limiting amino-acid in the proteins of wheat, maize, or oats? A., i, 185.
dietary deficiencies of the maize kernel, A., i, 192.
dietary deficiencies of the white bean, *Phaseolus vulgaris,* A., i, 363.
supplementary dietary relationship between leaf and seed as contrasted with combinations of seed with seed, A., i, 492.

McConnan, *James,* obituary notice of, T., 316.

McCourt, *Cyril Douglas,* obituary notice of, T., 318.

McCowan, *W.* See *Douglas Frank* **Twiss.**

McDanell, *Louise,* and *Frank Pell* **Underhill,** carbohydrate metabolism. XIV. Influence of administration of alkali on the sugar content of the blood in relation to the acid–base-producing properties of the diet. XV. Influence of acid-forming and base-forming diets on the sugar content of the blood, A., i, 359.
carbohydrate metabolism. XVIII. Relation of diet to the glycogen content of the liver, A., i, 364.
carbohydrate metabolism. XVI. Relation of adrenaline glycosuria to dosage and to the character of the diet. XVII. Influence of the intravenous injection of sodium carbonate on adrenaline hyperglycæmia and glycosuria, A., i, 368.
carbohydrate metabolism. XIX. Influence of the intravenous injection of sodium carbonate on the hyperglycæmia and glycosuria following the subcutaneous administration of dextrose, A., i, 368.
carbohydrate metabolism. XX. Mechanism of salt glycosuria, A., i, 368.

McDavid, *James Wallace,* the temperature of ignition of gaseous mixtures, T., 1003.

McDole, *Guy R.* See *Frederick Jacob* **Alway.**

McDonnell, *C. C.,* and *J. J. T.* **Graham,** decomposition of lead hydrogen arsenate by water, A., ii, 534.

McDonnell, *C. C.,* and *R. C.* **Roark,** occurrence of manganese in insect flowers and insect flower stems, A., i, 720.

McDonnell, *C. C.,* and *C. M.* **Smith,** arsenates of lead. II. Equilibrium in the system, $PbO-As_2O_5-H_2O$, A., ii, 33.
arsenates of lead. III. Basic arsenates, A., ii, 314.

MacDougall, (*Miss*) *Elizabeth, Alfred Walter* **Stewart,** and *Robert* **Wright,** phosphorescent zinc sulphide, T., 663; A., ii, 471.

MacDougall, *Frank Henry,* the Dieterici equation of state, A., ii, 366.

McGregor, *H. M.,* proteins of the central nervous system, A., i, 185.

McGuigan, *Hugh,* nature of the sugar in the blood, A., i, 359.
Fehling's solution in the estimation of blood-sugar, A., ii, 428.

McGuigan, *Hugh,* and *Ellison L.* **Ross,** peptone hypoglycæmia, A., i, 528.
estimation of the dextrose in the blood in reference to the condition in which it is present, A., ii, 548.

Mach, *Felix,* and *P.* **Lederle,** use of titanium trichloride in analytical practice, A., ii, 580.

Macht, *David I.,* and *Homer G.* **Fisher,** toxic action of opium alkaloids individually and in combination with each other on *Paramœcia,* A., i, 678.

MacInnes, *Duncan A.,* and *J. M.* **Braham,** heats of dilution. I. A calorimeter for measuring heats of dilution. II. The heat of dilution of 3*N*-ethyl alcohol, A., ii, 560.

MacIntire, *W. H., L. G.* **Willis,** and *W. A.* **Holding,** the divergent effects of lime and magnesia on the conservation of soil sulphur, A., i, 723.

McIntosh, *Douglas,* the formation of esters, A., i, 441.

Mack, *E.* See *Friend Ebenezer* **Clark.**

Mack, *E. L.,* electrolytic formation of perchlorate, A., ii, 256.

Mack, *E. L.* See also *Charles W.* **Bennett.**

Mackenzie, *John Edwin,* and *Sudhamoy* **Ghosh,** the optical rotation and cryoscopic behaviour of sugars dissolved in (*a*) formamide, (*b*) water. II., A., i, 79.

Macleod, *John James Rickard,* chemical evidence of the presence of glycogen-like polysaccharide in the liver-blood of diabetic animals, A., i, 524.

Macleod, *John James Rickard*, *M. E.* **Fulk**, *J. H.* **Davis**, and *R. W.* **Scott**, experimental glycosuria. XI. Retention of dextrose, A., i, 367.

Macleod, *John James Rickard*, and *D. H.* **Hoover**, experimental glycosuria. XII. Production of lactic acid in the blood following the injection of alkaline solutions of dextrose or of alkaline solutions alone, A., i, 426.

McMaster, *LeRoy*, and *F. B.* **Langreck**, the transformation of nitriles into amides by hydrogen peroxide, A., i, 334.

McNair, *James B.*, the consistency of pectin gels, A., i, 80.

McPherson, *A. T.*, granular calcium chloride as a drying agent, A., ii, 500.

McPherson, *A. T.* See also *James R.* **Bailey**.

MacPherson, *D. J.* See *W. R.* **Bloor**.

Macri, *V.*, reaction of manganese salts, A., ii, 511.

hydrogen peroxide, A., ii, 529.

Madelung, *Walter*, theory of the oxidation of benzidine in its significance for peroxydase investigations, A., i, 285, 708.

Madsen, *Erik Höst*, reactions with halogen-substituted acids. II. Action of sodium methoxide on monobromosuccinic acid, α-bromo*iso*butyric acid, β-bromobutyric acid, and α-bromopropionic acid, A., ii, 250.

Mäkinen, *Eere*, uralite from uralite-porphyrite from Pellinge, Finland, A., ii, 495.

März, *S.* See *G.* **Ramann**.

Maggi, *H.*, and *Gertrud* **Woker**, osazones from mixtures of formaldehyde and starch, A., i, 686.

Maggi, *H.* See also *Gertrud* **Woker**.

Mailhe, *Alphonse*, and *F. de* **Godon**, the catalytic decomposition of benzoyl chloride, A., i, 137.

catalytic hydrogenation with formic acid, and products of the catalytic condensation of ordinary acetone, A., i, 315.

transformation of secondary and tertiary aliphatic amines into nitriles, A., i, 686.

Maillard, *Louis C.*, identity of the synthetic humin substances with the natural humin substances, A., i, 251.

Maimeri, *Carlo*. See *Roberto* **Lepetit**.

Mains, *Gerald H.* See *Harrison Eastman* **Patten**.

Mair, *William*, preparation of deoxycholic acid, A., i, 442.

Maisch, *O.* See *Alexander* **Gutbier**.

Makaroff-Semljanski, *J.* See *Walther* **Borsche**.

Maksorov, *B. V.* See *Vladimir Vasilevitsch* **Tschelincev**.

Manasse, *Ernesto*, minerals from Monte Arco, Elba, Italy, A., ii, 485.

Mangam, *A. W.*, and *Solomon Farley* **Acree**, the preparation of β-glucose, A., i, 446.

Mangels, *C. E.* See *E. B.* **Forbes**.

Mannheim, *E.* See *Georg* **Frerichs**.

Mannheim, *Julie*. See *Hermann* **Grossmann**.

Mannich, *Carl*, methyl derivatives of morphine, A., i, 473.

synthesis of β-ketonic bases, A., i, 634.

Mannich, *Carl*, and *W.* **Geilmann**, detection of methyl alcohol by catalytic dehydrogenation, A., ii, 392.

Mansfield, *C. M.* See *Ralph* **Hoagland**.

Maquenne, *Léon*, and *Ém.* **Demoussy**, influence of mineral matters on the germination of peas, A., i, 530.

March, *A.*, kinetic theory of reaction velocity, A., ii, 196.

Marcus, *Jerome S.*, an improved Bunsen diffusion apparatus, A., ii, 409.

Marden, *John W.*, and (*Miss*) *Mary Violet* **Dover**, solubilities of several substances in mixed non-aqueous solvents. II., A., ii, 243.

Marden, *John W.* See also (*Miss*) *Mary Violet* **Dover**.

Markarjan, (*Mlle.*) *V.* See *J. S.* **Zalkind**.

Marker, *J.* See *B.* **Kramer**.

Marquina, *M.*, solubility of thymol in mixtures of water and glycerol, A., i, 689.

Marquina, *M.* See also *B.* **Cabrera**.

Marriott, *William McKim*. See *Harold Leonard* **Higgins**, and *John* **Howland**.

Marsh, *James Ernest*, and *O. C.* **Lye**, estimation of mercury in organic compounds, A., ii, 219.

Marshall, *J. T. W.* See *Sara Stowell* **Graves**.

Marshall, *M. J.* See *R. F.* **Ruttan**.

Martin, *F.* See *Lothar* **Wöhler**.

Martin, *Frederick H.* See *Donald Pritchard* **Smith**.

Martin, *Gerald Hargrave*. See *George* **Senter**.

Marvel, *C. S.* See *Alfred W.* **Homberger**, and *William Albert* **Noyes**.

Mascarelli, *Luigi*, isomerism of erucic, brassidic, and *iso*erucic acids; results obtained by the cryohydrate or eutectic method. V., A., i, 195.

Mason, *Edward H.* See *Victor John* **Harding**.

Mason, *Frederick Alfred.* See *Albert Theodore* **King.**

Mason, *Walter,* and *Richard Vernon* **Wheeler,** the "uniform movement" during the propagation of flame, T., 1044.

Massink, *A.*, double salt formation between nitrates and sulphates in aqueous solution, A., ii, 412.

Massol, *Gustave,* and *A.* **Faucon,** absorption of the ultra-violet rays by some chloro-derivatives of ethane, ethylene, and acetylene, A., ii, 188.
  absorption of the ultra-violet rays by the iodo-derivatives of methane, A., ii, 283.

Mathews, *Joseph Howard,* measurement of cryoscopic constants at elevated temperatures, A., ii, 356.
  redetermination of the heat of vaporisation of water, A., ii, 560.

Mathews, *Joseph Howard,* and *Alfred J.* **Johnson,** electrical conductivity of several salts in pyridine, A., ii, 289.

Mathews, *Joseph Howard, Ellis L.* **Krause,** and *Van L.* **Bohnson,** thermal chemistry of pyridine, A., ii, 238.

Mathews, *Joseph Howard,* and *Philip A.* **Ritter,** equilibrium in the system: mercuric iodide–pyridine, A., ii, 300.

Mathews, *Joseph Howard,* and *Samuel* **Spero,** equilibrium in the system: cupric chloride–pyridine, A., i, 518.

Mathews, *Joseph Howard,* and (*Miss*) *Mary Elvira* **Weeks,** effect of various substances on the photochemical oxidation of solutions of sodium sulphite, A., ii, 230.

Matsuno, *K.* See *Yuji* **Shibata.**

Matula, *Johann,* tables for the electromotive estimation of ion concentration, A., ii, 13.

Matula, *Johann.* See also *Wolfgang* **Pauli.**

Mauthner, *Ferdinand,* and *E.* **Mika,** the synthesis of aryl substituted fatty acids, A., i, 337.

Maver, *Mary E.*, Schneyer method for the estimation of lactic acid in urine, A., ii, 583.

Mawrov, *Franz,* and *M.* **Nikolov,** new sulphides of molybdenum, A., ii, 479.

Max, *Fritz.* See *Heinrich* **Biltz.**

Maxted, *Edward Bradford,* disodium nitrite, an additive compound of sodium nitrite and sodium, T., 1016.
  the synthesis of ammonia and the oxidation of ammonia to nitric acid, A., ii, 465.

Maxwell, *Harold L.*, dissociation of complex double salts in aqueous solutions, A., ii, 562.

Mayer, *Charles,* formation and properties of β-amino-ketones derived from aromatic imines, A., i, 89.
  condensation of acetone with imines, A., i, 144.
  action of the alkaline-earth chlorides on urinary acidity, A., i, 239.

Mayer, *Friedrich,* and *W. H.* **Schramm,** the hydrogen peroxide reaction for copper and the hydrolytic state of dilute copper sulphate solutions, A., ii, 334.

Mazé, *Pierre,* and *M.* **Ruot,** production of pyruvic acid by biochemical oxidation of lactic acid, A., i, 310.

Mazzetti, *C.* See *Nicola* **Parravano.**

Meacham, *Merle R.* See *Nathaniel Edward* **Loomis.**

Meader, *J. W.*, (*a*) cephaeline *iso*butyl ether and (*b*) cephaeline propyl ether and salts thereof, A., i, 91.
  preparation of cephaeline *iso*amyl ether and salts thereof, A., i, 348.
  cephaeline butyl ether and salts thereof, A., i, 410.
  preparation of cephaeline amyl ethers and salts thereof, A., i, 475.

Mecacci, *F.* See *Umberto* **Sborgi.**

Mechel, *Lukas von.* See *Emil* **Fischer.**

Medofski, *F.* See *Lionel Guy* **Radcliffe.**

Meek, *David B.*, absorption spectra of some polyhydroxyanthraquinone dyes in concentrated sulphuric acid solution and in the state of vapour, T., 969; A., ii, 558.

Mehler, *Ludwig.* See *Wilhelm* **Biltz.**

Meissner, *K. W.*, regularities in the spectra of neon and argon, A., ii, 61.

Meldola, *Raphael,* obituary notice of, T., 349.

Meldola, *Raphael, Henry Stennett* **Foster,** and *Reinald* **Brightman,** attempts to prepare asymmetric quinquevalent nitrogen compounds. I. 5-Aminosalicylic acid and related compounds, T., 533; A., i, 453.
  attempts to prepare asymmetric quinquevalent nitrogen compounds. II. Nitrated hydroxydiphenylamines, T., 546; A., i, 454.
  attempts to prepare asymmetric quinquevalent nitrogen compounds. III. Hydroxyphenylglycine, T., 551, A., i, 454.

Meldrum, *William Buell.* See *Theodore William* **Richards.**

Mendel, *Lafayette Benedict.* See *Maurice Hope* **Givens,** *Shigenobu* **Kuriyama,** and *Thomas Burr* **Osborne.**

Merki, *W.* See *Siegmund Reich.*

Merl, *Th.*, and *K.* **Lüft,** experiences with Mandel and Neuberg's catalytic method for elementary analysis, A., ii, 383.

Merreywether, *J. E.* See *Henry Droop* **Richmond.**

Merrill, *David R.*, and *Elliot Quincy* **Adams**, hydrolysis of acetanilide, A., ii, 457.

Merrill, *George Perkins*, and *J. E.* **Whitfield**, iron meteorite from Cookeville, Tennessee, A., ii, 150.
  the meteoric irons of Whitfield Co., Georgia, A., ii, 150.

Merrill, *Paul W.*, wave-lengths of the stronger lines in the helium spectrum, A., ii, 434.

Merton, *Thomas Ralph*, and *John William* **Nicholson**, phenomena relating to the spectra of hydrogen and helium, A., ii, 433.

Merwin, *Herbert Eugene.* See *Emmanuel George* **Zies.**

Metzler, *L. F.* See *P. L.* **Gainey.**

Meulen, *P. A. van der*, two so-called halloysites from Georgia and Alabama, A., ii, 177.

Meyer, *Emil.* See *Hugo* **Kauffmann.**

Meyer, *Gustave Morris.* See *Phœbus A.* **Levene.**

Meyer, *Hans*, and *Alice* **Hofmann**, pyrocondensations in the aromatic series. II., A., i, 641.

Meyer, *Richard*, and *Hans* **Wesche**, pyrogenic acetylene condensations. IV., A., i, 313.
  some products of the reduction of 5-nitro*iso*phthalic acid, A., i, 340.
  hemimellitic acid, A., i, 341.

Michaelis, *August*, and *C. A.* **Rojahn**, application of Friedel and Crafts' ketone synthesis to pyrazoles, A., i, 480.

Michaelis, *Leonor*, electrometric method of titration, and its application to the examination of gastric juices, A., ii, 228.

Michaud, *Félix*, mixtures, A., ii, 122.

Mieczyński, *Tadeusz.* See *Jan von* **Zawidzki.**

Mieleitner, *Karl*, crystallographic examination of diphenyl and its derivatives, A., i, 641.

Mika, *E.* See *Ferdinand* **Mauthner.**

Milikan, *J.*, the oxy-salts of the alkaline earth metal haloids; equilibria in ternary systems. I. and II., A., ii, 257, 572.

Miller, *C. W.* See *Alonzo Englebert* **Taylor.**

Miller, *E.* See *Joseph Christie Whitney* **Frazer.**

Miller, *Willet G.*, and *Cyril W.* **Knight**, occurrence of euxenite in South Sherbrooke Township, Ontario, A., ii, 538.

Millmann, *Seb.* See *Fritz* **Ephraim.**

Mills, *James Edward*, molecular attraction. XIII., A., ii, 165.

Mills, *James Edward*, molecular attraction. XIV. Specific heats of the elements and some energy changes, A., ii, 356.

Minot, *Anna S.* See *Willey* **Denis.**

Mito, *T.*, asymmetric hydrolysis of racemic polypeptides by killed bacteria, A., i, 679.

Mitscherlich, *Alexander*, the ignition point of detonating gas, A., ii, 199.

Mitter, *Prafulla Chandra*, and *Jnanendra Nath* **Sen**, action of phenylhydrazine on opianic, nitro-opianic, and phthalonic acids; some derivatives of hydrazo- and azo-phthalide, T., 988; A., i, 710.

Mixter, *William Gilbert*, calorimetry by combustions with sodium peroxide, A., ii, 123.

Mixter, *William Gilbert*, and *Frank Loyal* **Haigh**, the Penfield test for carbon, A., ii, 269.

Miyake, *Kōji*, nature of nitrification and ammonification, A., i, 244.
  the influence of various cations on the rate of absorption of ammonium ion by soil, A., i, 247.
  the nature of ammonification, A., i, 718.

Modrzejewski, *J.* See *Hermann* **Staudinger.**

Möller, *Svend*, and *Paul* **Pfeiffer**, lead diethyl compounds, A., i, 122.

Moeller, *W.*, ultra-microscopic investigation of tanning phenomena in jellies, A., ii, 132.
  internal and surface structures in jellies. I., A., ii, 132.
  rhythmic diffusion structures in gelatin-salt jellies. I., A., ii, 410.
  ultra-microscopic investigation of the tanning process in jellies, A., ii, 454.

Mörner, (*Graf*) *Carl Thore*, compounds derived from proteins by energetic treatment with nitric acid. III., A., i, 710.
  compounds derived from proteins by energetic treatment with nitric acid. IV. *p*-Nitrobenzoic acid as an oxidation product of proteins, A., i, 710.
  compounds derived from proteins by energetic treatment with nitric acid. V. Formation of oxalic acid from proteins and amino-acids, A., i, 711.

Moir, *James*, colour and chemical constitution; quantitative study of the phthaleins and of other fuchsone derivatives, A., ii, 349.

Moir, *James,* new applications of thymolphthalein and naphtholphthalein in the estimation of true neutrality in waters, including rapid methods for analysing limestone and ammonium salts, A., ii, 386.
  colour and chemical constitution. II. Spectra of the mixed phthaleins and of the sulphone-phthaleins. A., ii, 557.
Moles, *Enrique,* revision of the atomic weight of bromine; determination of the normal density of gaseous hydrogen bromide, A., ii, 200.
  the new values of the atomic weights of carbon and sulphur in the International Table for 1916, A., ii, 257.
Molisch, *Hans,* microchemistry of plants. IV. Organic lime-balls and siliceous bodies in *Capparis,* A., i, 505.
  microchemistry of plants. II. Orange-coloured hydathodes in *Ficus javanica.* III. Brown colouring matter of "golden-yellow" grapes, A., i, 506.
  microchemistry of plants. VIII. Readily crystallisable organic substance in *Linaria* species, A., i, 506.
  microchemistry of plants. VII. Serratulin, A., i, 507.
  microchemistry of plants. V. Detection of dissolved calcium compounds by means of sodium carbonate, A., ii, 387.
  microchemistry of plants. VI. Detection of lime by means of potassium hydroxide or a mixture of potassium hydroxide and carbonate, A., ii, 387.
Molliard, *Marin,* catalytic rôle of potassium nitrate in the alcoholic fermentation produced by *Aspergillus niger,* A., i, 73.
Momber, *Fr.* See *Alfred* **Wohl.**
Mong, *W. L.* See *William Lloyd* **Evans.**
Monnier, *A.,* reactions for distinguishing between perchlorates, periodates, percarbonates, persulphates, and perborates, A., ii, 98.
Monroe, *Kenneth Potter.* See *James* **Kendall.**
Montagne, *Pieter J.,* action of alcoholic potassium hydroxide on ketones. III. Action of alcoholic potassium hydroxide on halogenoamino-benzophenones and -benzhydrols, A., i, 35.
  nitration of 4-bromo- and 4-chlorobenzophenones, A., i, 36.
  oxidation of *o*-iodotoluene with potassium permanganate, A., i, 84.
Montagne, *Pieter J.,* action of an alcoholic solution of potassium hydroxide on ketones. IV. Action of alcoholic potassium hydroxide solution on halogeno–aminobenzophenones, A., i, 143.
  diazotisation of 4-bromo 4′-aminobenzophenone in alcoholic solution, A., i, 460.
Montequi Díaz de Plaza, *Ricardo,* cuprous *iso*butylxanthates, A., i, 249.
Monti, *P.* See *Paul* **Pfeiffer.**
Moore, *Arthur R.,* mechanism of cytolysis in sea-urchin eggs, A., i, 185.
  mechanism of cytolysis in echinoderm eggs. II., A., i, 493.
Moore, *Forris Jewitt,* and *Ruth M.* **Thomas,** the constitution of xanthogallol, A., i, 460.
Moore, *Hugh K., G. A.* **Richter,** and *W. B. van* **Arsdel,** incomplete hydrogenation of cotton-seed oil, A., i, 442.
Moore, *N. H.* See *James R.* **Bailey.**
Moore, *Robert J.* See *Gustav* **Egloff.**
Moore, *William,* toxicity of various benzene derivatives to insects, A., i, 527.
  volatility of organic compounds as an index of the toxicity of their vapours to insects, A., i, 678.
Moran, *J.,* the release of radium emanation from water at different temperatures by the bubbling method, A., ii, 63.
  a comparison of radium standard solutions (continued), A., ii, 230.
Moreau, *Edmond,* a new practical colorimeter, A., ii, 418.
Morey, *George W.,* a convenient form of autoclave, A., ii, 305.
Morey, *George W.,* and *Clarence N.* **Fenner,** the ternary system, H_2O–K_2SiO_3–SiO_2, A., ii, 370.
Morgan, *Agnes Fay,* the molecular rearrangement of some triarylmethylchloroamines, A., i, 21.
Morgan, *D. G.* See *O. C.* **Smith.**
Morgan, *Gilbert Thomas,* preparation of monoalkylated aromatic amines (*N*-alkylarylamines), A., i, 197.
Morgan, *Gilbert Thomas,* and *Henry Philip* **Tomlins,** the constitution of internal diazo-oxides (diazophenols). II., T., 497; A., i, 481.
Morgan, *Gilbert Thomas,* and *Adolph William Henry* **Upton,** acyl derivatives of paradiazoiminobenzene, T., 187; A., i, 300.
Morgan, *John Livingston Rutgers,* and *Ward V.* **Evans,** surface tensions of the co-existing layers of systems of mutually soluble liquids, A., ii 561.

Morgan, *L. E.* See *E. B.* **Forbes.**

Morgulis, *S.*, chemical constitution of chitin, A., i, 407.

Morosov, *V. A.*, function of calcium in the nutrition of garden pea seedlings with ammonium salts, A., i, 616.

Morozewicz, *Józef* [*Marian*], occurrence of native copper in the Komandor Islands, Bering Sea, A., ii, 483.

Morris, *J. Lucien*, quick titration method for estimating small amounts of uric acid, A., ii, 279.

Morriss, *W. H.* See *Yandell* **Henderson.**

Morrow, *Clarence Austin*, and *Ross Aiken* **Gortner**, the organic matter of the soil. V. The nitrogen distribution in different soil types, A., i, 512.

Morse, *Max*, enzyme and reaction of medium in autolysis, A., i, 526.
proteoclastic tissue enzymes of the spleen, A., i, 606.

Mortimer, *F. S.*, and *J. Newton* **Pearce**, electromotive forces and electrode potentials in pure and mixed solvents. II., A., ii, 289.

Mosbacher, the analysis of zinc alloys, A., ii, 389.
apparatus for the preparation of hydrogen sulphide or hydrogen, A., ii, 464.

Mosenthal, *Herman O.* See *Alma* **Hiller.**

Mostowitsch, *W.*, and *W.* **Pletneff**, volatility of gold at high temperatures in atmospheres of air and other gases, A., ii, 213.

Mott, *William Roy*, and *Clayton W.* **Bedford**, the flame arc in chemical manufacture, A., ii, 6.

Mougne, preparation of β-ethyl galactoside by means of the kernels of apricots, peaches, and cherries, the seeds of apples, and bitter-almond cake, A., i, 379.
β-galactosidase in the vegetable kingdom, A., i, 438.

Müller, *Arno*, explosive property of uranyl nitrate. II., A., ii, 373.

Müller, *E.* See *Julius von* **Braun.**

Müller, *Ernst*, detection of carbon in inorganic and organic substances, A., ii, 269.

Müller, *Friedrich C. G.*, electrolysis of hydrochloric acid in Hofmann's apparatus, A., ii, 463.
when is a candle extinguished in an enclosed volume of air? A., ii, 463.

Müller, *F. P.*, minerals from the manganese ore deposits of Oberhalbstein, Grisons, Switzerland, A., ii, 149.

Müller, *Hugo*, obituary notice of, T., 572.

Müller, *Ilse*, the basicity of hypophosphoric acid, A., ii, 30.

Müller, *Johannes*, and *Hans* **Murschhauser**, the physiological evaluation of the esters of fatty acids. I. Ethyl esters, A., i, 492.

Mueller, *J. Howard*, mechanism of cholesterol absorption, A., i, 65.
solubility of cholesterol-digitonide, A., ii, 393.

Müller, *R. F.* See *Georg* **Schroeter.**

Münter, *F.*, absorption and nitrification of ammonium compounds in the presence of zeolites in soil; estimation of ammonia in soil and on zeolithic substances, A., i, 722.
estimation of ammonia in soils, A., ii, 578.

Münzer, *E.*, and *W.* **Neumann**, the differential blood-gas apparatus of Barcroft, A., i, 520.

Muller, *Ch.*, Muller's process for the destruction of reducing principles, permitting of the direct estimation of crystallisable sugar, specially applicable to the products of the cane-sugar industry, A., ii, 222.

Muller, *Joseph Auguste*, the ionisation of sulphuric acid and neutral potassium sulphate in aqueous solutions of moderate concentrations, A., ii, 117.
some electrolyses, A., ii, 117.

Muller, *P.* See *A. A. Hymans van den* **Bergh.**

Mully, *H.* See *Paul* **Pfeiffer.**

Mumm, *Otto.* See *Andreas* **Knust.**

Muncie, *Fred Weaver.* See *George Denton* **Beal.**

Murakami, *Takejirô.* See *Kôtarô* **Honda.**

Murlin, *John Raymond*, and *L. F.* **Craver**, [with *Walter L.* **Niles**, and *Warren* **Coleman**], influence of sodium carbonate, administered by duodenal tube, on human diabetes, A., i, 104.

Murlin, *John Raymond*, and *B.* **Kramer**, pancreatic diabetes in the dog. I. Influence of alkali and acid on the glycosuria and hyperglycaemia, A., i, 69.

Murlin, *John Raymond*, and *B.* **Kramer**, [with *J. A.* **Riche**], pancreatic diabetes in the dog. III. Influence of alkali on the respiratory metabolism after total and partial pancreatectomy, A., i, 69.

Murlin, *John Raymond*, and *Joshua Edwin* **Sweet**, pancreatic diabetes in the dog. IV. Influence of pylorus exclusion and of gastrectomy on the effects of pancreatectomy, A., i, 104.

Murlin, *John Raymond*. See also *B.* **Kramer.**

Murmann, *Ernst*, modification of the gravimetric estimation of chlorine and silver, A., ii, 38.

Murray, (*Miss*) *R. R.* See *William Ridgeley* **Orndorff.**

Murray, *Wallace Jennings*, the normal density of hydrogen bromide gas, A., ii, 201.

Murschhauser, *Hans*. See *Johannes* **Müller.**

Mussgnug, *F.* See *Ludwig* **Vanino.**

Muttelet, *C. F.*, estimation of arsenic in beer and in dextrose, A., ii, 101.

Myers, *Chester Newton*. See *Nathaniel Edward* **Loomis.**

Myers, *F. B.* See *George Leslie* **Kelley.**

Myers, *James Eckersley*, boric anhydride and its hydrates, T., 172 ; A., ii, 204.

Myers, *Rollin G.* See *Leonard C.* **Scott.**

Myers, *Victor Caryl*, estimation of small amounts of sugar in urine, A., ii, 221.

Myers, *Victor Caryl*, and *John A.* **Killian**, animal diastases. I. The increased diastatic activity of the blood in diabetes and nephritis, A., i, 369.

Mylius, *Franz*, and *Eric* **Groschuff**, pure bismuth, A., ii, 37.

Mylius, *Franz*, and *Karl* **Hüttner**, platinum and illuminating gas, A., ii, 482.

N.

Nacken, *Richard*, velocity of crystallisation in under-cooled fusions, A., ii, 363.

Nagai, *I.* See *Keisaku* **Shibata.**

Name, *Ralph Gibbs van*, the temperature-coefficient of a heterogeneous reaction, A., ii, 411.

Name, *Ralph Gibbs van*, and *W. G.* **Brown**, an apparatus for determining freezing-point lowering, A., ii, 163.
  tri-iodide and tri-bromide equilibria, especially in cadmium solutions, A., ii, 455.

Nametkin, *S. S.*, (*Mlle.*) *E. A.* **Grekova**, and (*Mlle.*) *A. M.* **Chuchrikova**, oxidation of camphenilone, A., i, 151.

Nametkin, *S. S.*, and (*Mlle.*) *A. K.* **Rushenceva**, fenchylene, a new synthetic terpene, A., i, 152.

Neal, *Roland*. See *Stewart Woodford* **Young.**

Neidle, *Marks*, and *Jacob* **Barab**, dialysis. II. Hot dialysis of the chlorides of ferric iron, chromium, and aluminium, and the rapid preparation of their hydrated oxides, A., ii, 262.

Neidle, *Marks*, and *John N.* **Crombie**, oxidation-reduction reactions without the addition of acid. III. Ferrous chloride and potassium permanganate ; a new method for the preparation of colloidal hydrated ferric oxide, A., ii, 93.

Nekritsch, *L.* See *E.* **Grischkevitsch-Trochimovski.**

Nelson, *Burt E.*, the composition of neurokeratin, A., i, 61.

Nelson, *C. Ferdinand*, and *W. E.* **Burns**, calcium and magnesium content of normal urine, A , i, 104.

Nelson, *C. Ferdinand*, and *J. L.* **Williams**, urinary and fæcal output of calcium in normal men, together with observations on the hydrogen-ion concentration of urine and fæces, A., i, 103.

Nelson, *E. K.*, gingerol and paradol, A., i, 572.

Nelson, *John Maurice*, and *Ward V.* **Evans**, electromotive force developed in cells containing non-aqueous liquids, A., ii, 232.

Nelson, *John Maurice*, and *W. C.* **Vosburgh**, kinetics of invertase action, A., ii, 252.

Neogi, *Panchānan*, and *Tarini Charan* **Chowdhuri**, reduction of aliphatic nitrites to amines, T., 899 ; A., i, 686.

Neresheimer, *Heinrich*. See *Carl Dietrich* **Harries.**

Nesbitt, *C. T.*, estimation of manganese in high-speed steels, A., ii, 180.

Neubauer, *K.*, silicate fusion solutions, A., ii, 492.

Neuberg, *Carl*, and *Eduard* **Färber**, the presence of emulsin-like ferments separable from the cells of bottom yeast, and the absence of myrosin in Berlin top and bottom yeast, A., i, 501.
  the course of alcoholic fermentation in an alkaline medium. I. Cell-free fermentation in alkaline solutions, A., i, 502.

Neuberg, *Carl*. See also *Kemal* **Djenab.**

Neuffer, *Leonora*. See *Lauder William* **Jones.**

Neumann, *Bernhard*, black sulphur, A., ii, 464.

Neumann, *L.* See *Julius von* **Braun.**

Neumann, *W.* See *E.* **Münzer.**

Neun, *Dora E.* See *Henry Clapp* **Sherman.**

Neuwirth, *Isaac*, hourly elimination of certain urinary constituents during brief fasts, A., i, 366.

Newbery, *Edgar*, the hydration of ions and metal overvoltage, T., 470 ; A., ii, 355.

Newbery, *Edgar*, overvoltage tables. III. Overvoltage and the periodic law, A., ii, 12.
  overvoltage tables. IV. The theories of overvoltage and passivity, A., ii, 64.
  the theory of overvoltage, A., ii, 290.
Newbery, *Edgar*. See also (*Sir*) *Robert* **Hadfield.**
Nicaise, *Ch.* See *Jules Émile* **Verschaffelt.**
Nichols, *M. Starr*, the phenolsulphonic acid method for nitrates in waters rich in magnesium salts, A., ii, 421.
Nichols, *Raymond William*, obituary notice of, T., 319.
Nicholson, *John William*. See *Thomas Ralph* **Merton.**
Nicolardot, *Paul*, and *Jean* **Boudet**, the estimation of boric acid in special glasses, A., ii, 383.
Niementowski, *Stefan von*, and *Ed.* **Sucharda**, synthesis of 1:3:10-trihydroxybenzo-2:5-naphthyridine [1:3:10-trihydroxy-2:5-naphthadiazine] and its conversion into kynurenic acid, A., i, 477.
Nierenstein, *Maximilian*, synthesis of hydroxyquercetin, T., 4; A., i, 149.
Niggemann, *Hermann*. See *Konrad* **Schaefer.**
Niggli, *Paul*, table of Schoenflies's cubic space-lattices, A., ii, 129.
  equilibria between titanium dioxide and carbon dioxide, and between silica and carbon dioxide, in alkali, lime–alkali and alkali–aluminate fusions, A., ii, 211.
  uniform pressure, deformation pressure, and rock metamorphosis, A., ii, 457.
Nikitin, *N. I.*, heat of combustion of wood charcoal, A., ii, 66.
Nikolaev, *A. W.*, mineralogy of the Kyshtymsk Mountains, A., ii, 487.
Nikolov, *M.* See *Franz* **Mawrow.**
Niles, *Walter L.* See *John Raymond* **Murlin.**
Nissen, *Arvid E.*, and *Samuel L.* **Hoyt**, occurrence of silver in argentiferous galena ores, A., ii, 144.
Nitta, *Shigeharu*. See *Toshio* **Takamine.**
Njegovan, *Vladimir*, relationship of heat capacity to entropy, A., ii, 405.
Nolf, *P.*, interesting property of old solutions of fibrinogen, A., i, 420.
Noll, *Hermann*, estimation of dissolved oxygen in water in the presence of nitrites and organic substances, A., ii, 502.
Nolte, *Otto*, the soil and soil-solution, A., i, 621.
  gypsum as a fertiliser, A., i, 624.
  estimation of nitrogen by Kjeldahl's method, A., ii, 578.
Nolte, *Otto*, and *Erna* **Hahn**, action of frost on the soil, A., i, 621.
Nolte, *Otto*. See also *Paul* **Ehrenberg.**
Nomura, *Hiroshi*, the pungent principles of ginger. I. A new ketone, zingerone[4-hydroxy-3-methoxyphenylethyl methyl ketone] occurring in ginger, T., 769; A., i, 570.
Norbury, *F. G.* See *C. G.* **MacArthur.**
Norman, *William*, the hydrolysis of iron ammonium alum, A., ii, 94.
Northrop, *John H.*, rôle of yeast in the nutrition of an insect (*Drosophila*), A., i, 525.
Northrop, *John H.* See also *Jacques* **Loeb.**
Nottbohm, *Otto*, preparation of carboxydisulphonic acids from the bisulphite compounds of unsaturated aldehydes and malonic acid, A., i, 27.
Nouri, *Osman*. See *Emil* **Fischer.**
Noyes, *Arthur Amos*, and *Kebe* **Toabe**, the relative electrode potentials of tin and lead determined by equilibrium measurements with their perchlorates, A., ii, 438.
Noyes, *William Albert*, kinetic hypothesis to explain the function of electrons in the chemical combination of atoms, A., ii, 287.
Noyes, *William Albert*, and *C. S.* **Marvel**, cyanocarbethoxy-3:3-dimethyl*cyclo*pentanone [ethyl 2-cyano-1:1-dimethyl*cyclo*pentane-3-one-2-carboxylate], A., i, 455.
Nussbaum, estimation of traces of water in alcohol, A., ii, 215.

O.

Odaira, *Isao*, influence of acid radicles containing different secondary alkyls on the narcotic action of urethane, A., i, 81.
Odén, *Sven*, pectin substances. II. Algic and fucic acids, A., i, 379.
  pectin substances. I., A., i, 436.
Œchsner de Coninck, [*François*] *William*, alkaline earth oxalates, A., i, 195.
Œchsner de Coninck, *William*, and **Gerard**, the atomic weight of lead, A., ii, 33.
Oesper, *Ralph E.* See *Alfred R.* **Jayson**, and *Leo* **Roon.**
Oesterheld, *G.*, the melting point and heat of fusion of glucinum, A., ii, 89.

Oesterheld, *G.*, the alloys of glucinum with aluminium, copper, silver, and iron, A., ii, 89.

Oesterle, *Otto A.*, substance accompanying lapachol in greenheart wood, A., i, 505.

Oesterle, *Otto A.*, and *R.* **Kueny**, homoeriodictyol, A., i, 703.

Oganessian, *A.* See *Siegmund* **Reich**.

Ogilvie, *C. B.* See *M. L.* **Crossley**.

Ohle, *Heinz.* See *Siegmund* **Gabriel**.

Ohlgart, *Christian.* See *Theodor* **Curtius**.

Ohlsson, *Erik*, the estimation of β-hydroxybutyric acid in urine, A., ii, 51.

Okey, *Ruth.* See *George Denton* **Beal**.

Okuda, *Yuzuru*, and *T.* **Eto**, the form of iodine in marine algæ, A., i, 437.

Olie, *Jacob, jun.*, and *A. J.* **Byl**, Röntgen-investigation of allotropic forms, A., ii, 286.

Oliver, *C. B.* See *James Watson* **Bain**.

Olivier, *Simon Cornelis Johannes*, some derivatives of benzenesulphinic acid, A., i, 550.

Onnes, *Heike Kamerlingh*, methods and apparatus used in the cryogenic laboratory. XVII. Cryostat for temperatures between 27° and 55° (absolute), A., ii, 407.

Onnes, *Heike Kamerlingh*, *Claude Auguste* **Crommelin**, and *P. G.* **Cath**, isothermals of monatomic substances and their binary mixtures. XVIII. A preliminary determination of the critical point of neon, A., ii, 407.

Oosterhuis, *E.* See *G.* **Holst**.

Opolski, *St.*, *L.* **Czaporowski**, and *J.* **Zacharski**, desmotropic forms of bromocyanophenylpyruvic esters, A., i, 29.

Opolski, *St.*, *Z.* **Kowalski**, and *J.* **Pilewski**, salts and esters of the nitrophenylacetonitriles, A., i, 25.

Oppenheim, *Kurt.* See *Carl Dietrich* **Harries**.

Oppenheimer, *Ruth.* See *Alexander O.* **Gettler**.

Orechov, *Alex. P.*, synthetic investigations in the indene series, A., i, 127.
  syntheses in the indene series. II. Synthesis of diphenylindene, A., i, 450.

Orechov, *Alex. P.*, and (*Mlle.*) *R.* **Grinberg**, syntheses in the indene series. III. Synthesis of phenylbenzylindene, A., i, 450.

O'Riordan, *W. M.* See *Hugh* **Ryan**.

Orlik, *W.*, estimation of zinc by Schaffner's method, A., ii, 333.

Orndorff, *William Ridgeley*, and *J. J.* **Kennedy**, the nitration products of phenoltetrachlorophthalein and some of their derivatives, A., i, 31.
  the nitration products of tetrachlorofluoran and some of their derivatives, A., i, 347.

Orndorff, *William Ridgeley*, and (*Miss*) *R. R.* **Murray**, a new class of phthaleins (mixed phthaleins) formed by heating *o*-4-hydroxybenzoylbenzoic acid with phenols, A., i, 339.

Orndorff, *William Ridgeley*, and (*Miss*) *R. R.* **Murray**, [with *H. C.* **Allen**], diphenyltetrachlorophthalide and some of its derivatives, A., i, 338.

Orndorff, *William Ridgeley*, and *C. C.* **Rose**, diethylamino-*m*-hydroxybenzoyltetrachlorobenzoic acid and trichlorodiethylaminoxanthonecarboxylic acid and some of their derivatives, A., i, 30.

Orr, (*Miss*) *Annie Mary Bleakly*, *Robert* **Robinson**, and (*Miss*) *Margaret Mary* **Williams**, action of halogens on piperonaldehyde, T., 946; A., i, 703.

Os, *D. van*, estimation of iodine in mineral water and in the thyroid gland, A., ii, 267.

Osborne, *Thomas Burr*, and *Charles Samuel* **Leavenworth**, protein copper compounds, A., i, 98.

Osborne, *Thomas Burr*, and *Lafayette Benedict* **Mendel**, growth of rats on diets of isolated food substances, A., i, 238.

Osborne, *Thomas Burr*, and *Lafayette Benedict* **Mendel**, [with *Edna L.* **Ferry**, and *Alfred John* **Wakeman**], relative value of certain proteins and protein concentrates as supplements to corn gluten, A., i, 237.
  rôle of vitamines in the diet, A., i, 603.

Osborne, *Thomas Burr*, and *Alfred John* **Wakeman**, new constituents of milk. II. The distribution of phosphatides in milk, A., i, 103.

Osterhout, *Winthrop John Vanleuven*, specific action of barium, A., i, 373.
  a dynamical theory of antagonism, A., i, 434.
  antagonism and Weber's law, A., i, 434.
  the penetration of balanced solutions and the theory of antagonism, A., i, 435.
  permeability and viscosity, A., i, 435.
  temperature-coefficients of life processes, A., i, 715.

Ostromisslenski, *Ivan von*, polymerisation of isoprene, divinyl, and dimethylerythrene to caoutchouc or its homologues, A., i, 399.
  preparation of substances equivalent to ebonite, celluloid, or guttapercha; synthesis of vulcanised caoutchouc, A., i, 403.
  synthesis of the symmetrical chloride and of the higher chloride of erythrene caoutchouc; new chlorides of natural isoprene and erythrene caoutchoucs, A., i, 404.
Ostwald, *Wilhelm*, absolute system of colours. II., A., ii, 281.
Ostwald, *Wolfgang*, the significance of electrolytes in processes of imbibition, A., i, 99.
Otsuka, *Ichiro*, bacterial decomposition of polypeptides, A., i, 369.
Outcault, *Harry E.* See *Orland R.* **Sweeney.**

P.

Paal, *Carl*, [with *Ferd.* **Biehler**, and *Hermann* **Steyer**], colloidal metals of the platinum group. IV. Colloidal iridium, A., ii, 375.
Paal, *Carl*, and *Max* **Hubaleck**, steric hindrance of chemical reactions. III. ψ-Cumylsulphamic acid (ψ-cumylaminosulphonic acid), A., i, 643.
  ψ-cumylnitrosoaminosulphonic acid, A., i, 644.
Paderi, *Cesare*, behaviour of dimethyleneglueonic acid and methylenesaccharic acid in the organism, A., i, 716.
Pagliani, *Stefano*, relations between thermal properties; molecular coefficient and constitution of organic compounds, A., ii, 120.
Paine, *Harry M.* See *William Draper* **Harkins.**
Palet, *Luciano P. J.*, a source of error in the investigation of urinary indoxyl, A., ii, 553.
  use of alkalis in quantitative analytical investigations, A., ii, 555.
Palkin, *Samuel*, separation of lithium from the other alkali metals, A., ii, 43.
  separation of aluminium from iron by means of ether, A., ii, 581.
Palkin, *Samuel*. See also *William O.* **Emery.**
Palmer, *Howard Earle.* See *Isaac King* **Phelps.**
Palmer, *Leroy S.* See *C. H.* **Eckles.**
Palmer, *Walter W.*, concentration of dextrose in the tissues of normal and diabetic animals, A., i, 494.
Panzer, *A.* See *Alfred* **Heiduschka.**
Paolini, *Vincenzo*, and *Giovanni* **Rebora**, isomeric sabinols, A., i, 90.
Pape. See *Max* **Cremer.**
Paris, *Giulio*, biochemistry of tobacco. I. Critical examination of the methods of estimating nitrogenous substances in tobacco leaves, A., ii, 227.
Parker, *Karr.* See *Edward Wight* **Washburn.**
Parker, *Reginald George*, the estimation of free sulphur trioxide in fuming sulphuric acid by titration with water, A., ii, 420.
Parravano, *Nicola*, and *Pietro de* **Cesaris**, heat of formation of ferrous sulphide, A., ii, 292.
Parravano, *Nicola*, and *C.* **Mazzetti**, cooling curves of ternary and quaternary mixtures, A., ii, 292.
Parsons, *Charles Lathorp*, preparation of black oxide of uranium (UO_2), A., ii, 373.
Partsch, *Fr.* See *B.* **Stuber.**
Pascal, *Paul*, normal and acid sodium sulphates, A., ii, 248.
  the distillation of mixtures of nitric and sulphuric acids, A., ii, 569.
Pasternack, *Richard.* See *Paul* **Rabe.**
Patten, *Harrison Eastman*, and *Gerald H.* **Mains**, an apparatus for the purification of mercury, A., ii, 413.
Patterson, *Thomas Stewart*, the influence of solvents, etc., on the rotation of optically active compounds. XXI. The relationship of the rotatory powers of ethyl tartrate, *iso*butyl tartrate, and *iso*butyl diacetyltartrate, A., ii, 3.
  the influence of solvents, etc., on the rotation of optically active compounds. XXII. Rotation dispersion, A., ii, 4.
  the influence of solvents, etc., on the rotation of optically active compounds. XXIII. Anomalous rotation-dispersion and dynamic isomerism, A., ii, 5.
Paul, *J. H.*, and *John Smith* **Sharpe**, calcium metabolism. I. Deposition of lime salts in the integument of decapod crustacea, A., i, 66.
Paul, *Ludwig*, ammonium soaps of colophony, A., i, 214.
Paul, *Theodor*, the connexion between acid taste and hydrogen-ion concentration, A., i, 75.
  physical chemistry of foods. II. Reduction of the acidity of wine with calcium carbonate (chaptalising); tartaric acid and its salts, A., i, 246.

Paul, *Theodor*, physical chemistry of foods. III. The chemical equilibrium between tartaric acid and potassium tartrate as basis of the reduction of the acidity of wine by means of this salt, A., i, 507.

physical chemistry of foods. IV. Scientific wine tests to determine the relationship between the strength of the acid taste and the hydrogen-ion concentration, A., i, 509.

a thermostat for polarimetric [determinations] particularly during sugar inversion at high temperatures, A., ii, 5.

Pauletig, *Marius*, digestibility of starches from various vegetable foods by the diastases from malt, pancreas, and saliva, A., i, 670.

Pauli, *Wolfgang*, and *Johann* **Matula**, physical changes in the condition of colloids. XXI. Protein silver salts, A., i, 419.

physico-chemical analysis of colloidal ferric hydroxide, A., ii, 563.

Pauli, *Wolfgang*. See also *Albert* **Fernau.**

Paulsen, *Edgar*. See *Carl Dietrich* **Harries.**

Pauly, *Hermann*, synthesis of peptides in the animal organism, A., i, 525.

Pavlov, *P. N.*, molecular condition of pure liquids, A., ii, 125, 293, 358.

Peachey, *Stanley John*, catalytic acceleration of the vulcanising process, A., i, 406.

Pearce, *J. Newton*. See *F. S.* **Mortimer.**

Pearce, *W. Tudor*. See *William Draper* **Harkins.**

Pearson, (*Mrs.*) *Leonore Kletz*. See *Arthur* **Lapworth.**

Pecker, *Henri*, detection of picric acid and its derivatives, A., ii, 158.

Pekarskaja, (*Mlle.*) *G. F.* See *Michael A.* **Rakuzin.**

Pellet, *Henri*, nature of the reducing substances precipitated by basic lead acetate from impure sugar solutions, A., i, 8.

the influence of pentoses in the estimation of reducing sugars by means of our new method of heating at 63–65° for ten minutes (mixture of the cupropotassic solution and the liquid to be analysed), A., ii, 222.

the estimation of reducing sugars in the sugar cane molasses and in the fermented liquid of these molasses or the determination of the fermented sugars, A., ii, 222.

glutose, A., ii, 223.

Pellet, *Henri*, direct polarisation of sugar solutions without a preliminary treatment with basic lead acetate or the normal acetate, A., ii, 428.

estimation of potassium and sodium in vegetable ashes, A., ii, 542.

Pellini, *Giovanni*, esters of telluric acid, A., i, 2.

Pelloux, *Alberto*, variscite from Sarrabus, Sardinia, A., ii, 490.

Penfold, *A. R.* See *Richard W.* **Challinor.**

Pérard, *Joseph*, certain derivatives of *p*-dialkylamino-*o*-benzoylbenzoic acids, A., i, 651.

Pérégrin, *J. B.*, registering apparatus for the estimation of excess of oxygen in lead-chamber cases, A., ii, 39.

Lunge's method for the rapid estimation of sulphur in roasted ores, A., ii, 179.

Lunge's method for the rapid estimation of arsenic in sulphuric acid, A., ii, 180.

Pereira-Forjaz, *A.*, spectrographic studies of some Portuguese uranium and zirconium minerals, A., ii, 113.

Perkin, *William Henry, jun.*, cryptopine and protopine, A., i, 280.

Perkins, *R. L.*, estimation of alcohol and water in ether for anæsthesia, A., ii, 393.

Perley, *G. A.*, and *Charles W.* **Davis**, reduction of lead sulphate, A., ii, 141.

Perlmutter, *S. I.* See *Nicolai S.* **Kurnakov.**

Perrot, *François Louis*, measurement of surface tension by the method of the weight of drops, A., ii, 408.

Pervier, *N. C.* See *G. P.* **Plaisance.**

Peskov, *N. P.*, quantitative light-filter for the ultra-violet part of the spectrum, A., ii, 349.

Peter, *A. M.* See *Philip Lee* **Blumenthal.**

Peters, *Charles Adams*, and *L. E.* **Fielding**, oxalate-iodide process for Paris green analysis, A., ii, 104.

Petersen, *Agnes*. See *Emil* **Baur.**

Petherd, *Victor Petheou.de.* See *Adolf* **Kaufmann.**

Petridis, *Georg*. See *Theodor* **Curtius.**

Pfannenstiel, *Hugo*. See *Wilhelm* **Wislicenus.**

Pfau, *Alexander*. See *Josef* **Houben.**

Pfeiffer, *Paul*, 3:4-benzofluorenone, A., i, 145.

crystals as molecular compounds. II., A., ii, 78.

Pfeiffer, *Paul*, and *Joseph* **Grimmer**, chromanones; the brazilin question. I., A., i, 661.

Pfeiffer, *Paul*, [with *W.* **Jowleff**, *Ph.* **Fischer**, *P.* **Monti**, and *H.* **Mully**], coloured organic molecular compounds, A., i, 205.
Pfeiffer, *Paul*, [with *J.* **Klinkert** and *A. von* **Pollitzer**], the border-line between isomerism and polymorphism. II., A., i, 140.
Pfeiffer, *Paul*, *P.* **Truskier**, and *P.* **Disselkamp**, organo-lead compounds, A., i, 122.
Pfeiffer, *Paul*. See also *Svend* **Möller**.
Phelps, *Earle Bernhard*, and *H. L.* **Shoub**, estimation of nitrate in sewage by means of *o*-tolidine, A., ii, 504.
Phelps, *Isaac King*, and *Howard Earle* **Palmer**, separation and estimation of butyric acid in biological products. I., A., ii, 278.
  the identification and estimation of lactic acid in biological products, A., ii, 278.
Phillips, *Harcourt*, volumetric estimation of sulphur in pyrites, A., ii, 379.
Piccard, *Jean*, and *Louis M.* **Larsen**, the three nitrotriphenylamines, A., i, 644.
Pickering, *Spencer Percival Umfreville*, the detergent action of soap, T., 86; A., ii, 165.
  problems bearing on residual affinity, A., ii, 528.
Pictet, *Amé*, *O.* **Kaiser**, and *A.* **Labouchère**, the alcohols and bases of vacuum tar, A., i, 515.
Pieck, *Marianne*. See *Arthur* **Rosenheim**.
Pieper, *Ernest J.*, *Solomon Farley* **Acree**, and *C. J.* **Humphrey**, chemical composition of the higher fractions of maplewood creosote, A., i, 452.
Pigulevski, *G. V.*, investigation of the influence of climatic conditions on the composition of plant oils, A., i, 189.
Pihlblad, *Nils*, a new proof of the existence of molecules. VI. The absorption of light by molecular and colloidal solutions of sulphur, A., ii, 557.
Pilat, *St. von*. See *Georg von* **Kozicki**.
Pilewski, *J.* See *St.* **Opolski**.
Pilz, *Ferdinand*, action of radium on plants in water cultures, A., i, 718.
Piña de Rubies, *Santiago*, presence of nickel and cobalt in chromites, A., ii, 214.
Pincussohn, *Ludwig*. See *Erich* **Leschke**.
Pinnow, *Johannes*, sulphonation of quinol. II., A., ii, 528.
Pinsker, *Jacob*. See *Arthur* **Rosenheim**.
Piotrowski, *J.* See *Julius* **Tröger**.
Pischtschimuka, *P. S.*, biological syntheses: *p*-hydroxyphenylethanol (tyrosol), A., i, 87.
Pitz, *Walter*. See *Elmer Verner* **McCollum**.
Plachuta, *N. I.* See *Vassili V.* **Scharvin**.
Plaisance, *G. P.*, the occurrence of *l*-leucine in sweet clover silage, A., i, 721.
  thiobarbituric acid as a qualitative reagent for ketohexose, A., ii, 276.
Plaisance, *G. P.*, and *N. C.* **Pervier**, simple device for evaporating solutions to a definite volume, A., ii, 378.
Plaisance, *G. P.* See also *Arthur Wayland* **Dox**.
Plass, *E. D.* See *D. Wright* **Wilson**.
Plato, *Wilhelm*. See *Otto* **Ruff**.
Pletneff, *W.* See *W.* **Mostowitsch**.
Plotnikov, *Vladimir Alexandrovitsch*, [with **Salatko-Petrischtsche**], preparation of carbonyl chloride, A., ii, 138.
Plum, *H. M.* See *Fred. W.* **Upson**.
Poch, *P.* See *Julio de* **Guzmán Carrancio**.
Podszus, *Emil*, plasticity, A., ii, 245.
  velocity of reaction in heterogeneous systems and size of granules, A., ii, 300.
  the preparation in a pure state of highly reactive metals and metalloids, A., ii, 373.
  fusion of zirconium dioxide and the preparation from it of apparatus, A., ii, 480.
Pohl, *Julius*, purine metabolism after poisons, A., i, 498.
Pokorny, *Jos.*, qualitative spectrum analysis of organic dye-stuffs by Formánek's method, A., ii, 402.
Polak, *James Jozef*, value of the determination of the freezing-point in the examination of milk, A., ii, 279.
Pollak, *Rudolf*. See *Alfred* **Eckert**.
Pollitz, stable starch solution, A., ii, 498.
Pollitzer, *A. von*. See *Paul* **Pfeiffer**.
Polonovski, *Max*, the alkaloids of the Calabar bean. VI. Constitution of geneserine; transformation of eserine into geneserine, A., i, 706.
Pomilio, *Umberto*, electrolytic oxidation of cresols [preparation of salicylic acid], A., i, 332.
Pooth, *Peter*, colour reactions of aromatic aldehydes, A., ii, 52.
Popesco, *Alin*, detection of ferrous salts in body fluids by means of the phosphotungstic reagent, A., ii, 44.
Poplawski, *Wladislaus*. See *Friedrich* **Kehrmann**.

Porges, *Otto*, the "reduced" and "regulated" hydrogen number of the blood, A., i, 64.

Porter, *Agnes Ellen*, distribution of esterases in the animal body, A., i, 238.

Porter, *Lyman E.* See *Percy Embury* **Browning.**

Portevin, *A.*, manganese steels, A., ii, 415.
  the carburation of iron by alkali cyanides and cyanates, A., ii, 476.

Portevin, *A.*, and **Garvin**, influence of the velocity of cooling on the temperature of transformation and structure of carbon steels, A., ii, 372.

Portevin, *A.* See also **Garvin.**

Posen, *I.* See *Richard* **Lorenz.**

Potjan and **Steffenhagen**, detection of albumin by bleaching powder solution and hydrochloric acid, A., ii, 520.

Potter, *Ralph S.*, and *T. H.* **Benton**, organic phosphorus of the soil, A., i, 76.

Potter, *Ralph S.*, and *R. S.* **Snyder**, soluble non-protein nitrogen of the soil, A., i, 75.

Powell, *A. D.*, estimation of small quantities of cobalt, A., ii, 220.

Powell, *A. R.* See *Walter R.* **Schoeller.**

Poyarkov, *E.*, applicability of Schulze's law to complement, A., i, 427.

Prager, *W.* See *Lothar* **Wöhler.**

Pratt, *L. S.*, an efficient desiccator, A., ii, 255.

Preis, *K.* See *František* **Slavík.**

Prescher, *J.*, separation of cholesterol and phytosterol from fats and oils by means of digitonin, A., ii, 275.
  separation of phytosterol and cholesterol (from fats and oils) and the digitonin-precipitation method of Marcusson and Schilling, A., ii, 514.

Prianichnikov, *Dmitri N.*, rôle of ammonia in the metabolism of nitrogenous substances in plants, A., i, 616.

Prideaux, *Edmund Brydges Rudhall.* See *Edward de Wyckersley Swyft* **Colver.**

Prim, *Aug.*, separation of antimony and tin by hydrogen sulphide in hydrochloric acid solution, and their iodometric estimation, A., ii, 392.

Prins, *Ada.* See *Ernst Hendrik* **Büchner.**

Prins, *H. J.*, isomerisation, polymerisation, and formation of additive products of α-pinene, A., i, 90.
  isomerisation and hydration of citronellaldehyde by acids, A., i, 513.
  a simple demonstration of the addition of water to terpineol under the influence of acids, A., i, 518.

Prins, *H. J.*, two isomeric citronellaldehydes, A., i, 538.
  relation between odour and constitution, A., i, 607.
  condensation of unsaturated systems, A., i, 685.

Pritchett, *R. H.* See *Eugene Paul* **Schoch.**

Pritzker, *J.*, cryoscopy and refractometry of milk, A., ii, 549.

Procopiu, *St.*, the concentration of the electrolytes in the neighbourhood of the electrodes, A., ii, 291.

Procter, *Henry Richardson*, and *John Arthur* **Wilson**, theory of vegetable tanning, A., i, 91.

Prosad, *Nogendra.* See *Rasik Lal* **Datta.**

Prud'homme, *Maurice*, the theoretical existence of a second critical point, A., ii, 192.

Puchner, *H.*, investigation of soil excrescences, A., i, 532.

Pulsifer, *H. B.*, estimation of sulphur in iron and steel, A., ii, 100.

Purdie, *Thomas*, obituary notice of, T., 359.

Purvis, *John Edward.* See *Charles Stanley* **Gibson.**

Pyman, *Frank Lee*, relation between chemical constitution and physiological action in certain substituted aminoalkyl esters. II., T., 167; A., i, 304.
  alkaloids of ipecacuanha. II., T., 419; A., i, 410.
  the relation between chemical constitution and physiological action, T., 1103.

Q.

Quirke, *Terence T.*, and *Leo* **Finkelstein**, measurements of the radioactivity of meteorites, A., ii, 576.

R.

Rabe, *Paul*, and *Bruno* **Böttcher**, cinchona alkaloids. XVIII. α-*iso*Cinchonine, A., i, 281.

Rabe, *Paul*, [with *Richard* **Pasternack**], the cinchona alkaloids. XVII. Degradation of cincholeupone to 4-aminomethyl-3-ethylpiperidine, A., i, 216.

Rabe, *Paul*, *Richard* **Pasternack**, and *Karl* **Kindler**, 4-quinolyl ketones. III. Synthesis of substances related to quinine, A., i, 283.

Rabinovitz, *Louis.* See *Carleton* **Ellis.**

Radcliffe, *Lionel Guy,* and *F.* **Medofski,** examination of acetic anhydride, A., ii, 397.

Radford, (*Mrs.*) *Norah,* and *G.* **Brewer,** estimation of theobromine, A., ii, 519.

Rae, *William Norman,* a period of induction in the dehydration of some crystalline hydrates, A., ii, 24.

Rae, *William Norman.* See also *Alfred Francis* **Joseph.**

Raffety, *Charles W.,* the spectra of carbon and hydrocarbon, A., ii, 61.

Raffo, *Mario,* and *O.* **Balduzzi,** action of pyridine and of piperidine on certain organic sulphur compounds. III., A., i, 382.

Rainy, *Harry,* and *Christina M.* **Hawick,** clinical methods of estimation of sugar in blood, A., ii, 49.

Raistrick, *Harold,* new type of chemical change produced by bacteria; conversion of histidine into urocanic acid by bacteria of the *Coli-typhosus* group, A., i, 499.

Rakshit, *Jitendra Nath,* titration and estimation of morphine with iodic acid, A., ii, 553.

Rakuzin, *Michael A.,* relation between filtration of the [solid] paraffins of naphtha and their adsorption, A., i, 109.

  irreversible adsorption of the "carbonaceous substances" of petroleum, A., i, 109.

  optical activity of albuminates of the alkali metals, A., i, 180.

  new classification of the processes of adsorption and importance of the theory of adsorption for various branches of natural science; adsorption of solutions by porous substances, A., ii, 72.

  behaviour of ferric oxide and hydroxide towards aqueous solutions of hen's egg-albumin, A., ii, 72.

  protein substances and anti-substances as products of adsorption, A., ii, 124.

  optical activity of proteins, enzymes, toxins, and serums, A., ii, 286.

  comparative adsorption of sucrose, inulin, and dextrin, A., ii, 294.

Rakuzin, *Michael A.,* and (*Mlle.*) *Ek. Maks.* **Braudo,** rotatory power of nucleic acids and of nucleates of the alkali metals, A., i, 99.

  optical activity of gelatinates of the alkali metals: chemistry of α- and β-gelatins, A., i, 181.

Rakuzin, *Michael A.,* and (*Mlle.*) *Ek. Maks.* **Braudo,** aluminium oxide and hydroxide as adsorbents and their behaviour towards aqueous solutions of hen's egg-albumin, A., ii, 73.

  influence of the quantity of the adsorbent, aluminium hydroxide, on the adsorption of aqueous solutions of hen's egg-albumin of constant concentration, A., ii, 124.

Rakuzin, *Michael A.,* and *G. D.* **Flier,** adsorption of toxins and antitoxins by aluminium hydroxide: Koch's tuberculin. I., A., i, 181.

  optical properties of diastase and its adsorption by kaolin and by aluminium hydroxide, A., i, 181.

  specific gravity of aqueous solutions of hen's egg-albumin, A., i, 232.

  selective adsorption of anti-diphtheritic serum by aluminium hydroxide, A., i, 427.

  selective adsorption of Denys's tuberculin by aluminium hydroxide, A., i, 428.

Rakuzin, *Michael A., G. D.* **Flier,** and *M. A.* **Bloch,** limiting concentrations in the adsorption of aqueous solutions of hen's egg-albumin by aluminium hydroxide; stoicheiometry of processes of adsorption, A., ii, 73.

Rakuzin, *Michael A.,* and (*Mlle.*) *G. F.* **Pekarskaja,** adsorption of alkannin in different solvents, A., i, 153.

  legumin as the analogue of casein, A., i, 232.

  optical and other properties of pancreatin, A., i, 422.

Ramann, *Emil,* and *A.* **Spengel,** the exchange of bases in silicates. I. The exchange of alkalis and ammonia in hydrated alumina alkali silicates (permutites), A., ii, 468.

Ramann, *G., S.* **März,** and *H.* **Bauer,** soil solution obtained by the action of a hydraulic press, A., i, 311.

Ramart-Lucas, (*Mme.*) *Pauline.* See *Albin* **Haller.**

Ramsay, *Arthur Alexander,* the solubility of calcium phosphates in citric acid, A., ii, 413.

Ramsay, (*Sir*) *William,* obituary notice of, T., 369.

Randall, *Merle.* See *Gilbert Newton* **Lewis.**

Rao, *Basrur Sanjiva.* See *Francis Lawry* **Usher.**

Rasmussen, *H. Baggesgaard,* exact estimation of atropine, A., ii, 431.

Rather, *J. B.,* the inositol phosphoric acids of cottonseed meal, A., i, 315.

Rathgen, *F.*, composition of a bronze age wind instrument, A., ii, 316.
Rathsburg, *Hans.* See *Otto* **Ruff.**
Ratner, *S.*, the distribution of the active deposit of radium in an electric field, A., ii, 558.
Rau, *Madyar Gopala.* See *Charles Stanley* **Gibson,** and *John Lionel* **Simonsen.**
Ravenna, *Ciro.* See *Giacomo Luigi* **Ciamician.**
Rây, *Prafulla Chandra*, mercury mercaptide nitrites and their reaction with the alkyl iodides. III. Chain compounds and sulphur, T., 101; A., i, 194.
  cadmium and zinc nitrites, T., 159; A., ii, 208.
  alkaloidal derivatives of mercuric nitrite, T., 507; A., i, 470.
Rây, *Prafulla Chandra*, and *Manik Lal* **Dey,** synthesis of αβ-thiocrotonic acid, T., 510; A., i, 441.
Rây, *Prafulla Chandra*, *Manik Lal* **Dey,** and *Jnanendra Chandra* **Ghosh,** velocity of decomposition and the dissociation constant of nitrous acid, T., 413; A., ii, 301.
Ray, *R. C.* See *Morris William* **Travers.**
Rayleigh, *Lord*, the Le Chatelier-Braun principle, T., 250; A., ii, 236.
Rea, *Renzo*, isomorphism of nitrates and chlorates, A., i, 633.
Read, *B. E.*, guanine-mononucleotide (guanylic acid) and its preparation from yeast-nucleic acid, A., i, 596.
Read, *B. E.*, and *W. E.* **Tottingham,** tritico-nucleic acid, A., i, 596.
Read, *B. E.* See also *Walter* **Jones.**
Read, *John*, and (*Miss*) *Margaret Mary* **Williams,** action of bromine water on ethylene, T., 240; A., i, 313.
Rebière, *Georges*, silver electro-colloids, A., ii, 571.
Rebora, *Giovanni.* See *Vincenzo* **Paolini.**
Reddelien, *Gustav*, filtration with the exclusion of moisture and air, A., ii, 461.
Redgrove, *Herbert Stanley*, a contribution to the energy theory of matter, A., ii, 411.
Reed, *Guilford B.*, relation of oxydase reactions to changes in hydrogen ion concentration, A., i, 62.
  the measurement of oxidation potential and its significance in the study of oxydases, A., i, 358.
  mechanism of oxydase action, A., i, 423.
  mode of action of plant peroxydases, A., i, 424.
  the relation between oxydase and catalase in plant tissues, A., i, 424.
Reed, *Guilford B.*, significance of colour changes in oxydase reagents; separation of oxydase reactions from the catalase reaction, A., i, 424.
Reed, *J. C.* See *C. B.* **Holland.**
Regenbogen, (*Mej.*) *A.* See *Nicolaas* **Schoorl.**
Reich, *Siegmund*, ring formation with the elimination of a nitro-group, A., i, 585.
Reich, *Siegmund*, [with *G.* **Gaigailian** and *P.* **Chaskelis**], phenyl-2:6-dinitrobenzylhydrazine, A., i, 595.
Reich, *Siegmund*, and *A.* **Oganessian,** some 2:6-dinitrobenzyl derivatives, A., i, 554.
Reich, *Siegmund*, and *W.* **Merki,** a method of formation of 6:6′-dichloro-2:2′-azobenzoic acid, A., i, 227.
Reich, *Siegmund*, and (*Mlle.*) *Bronislava* **Turkus,** ring formation with the elimination of a nitro-group, A., i, 585.
Reichel, *Frank H.* See *Richard Edwin* **Lee.**
Reid, *Ebenezer Emmet*, the identification of phenols, A., i, 333.
  the identification of acids, A., i, 333.
  studies in identification. IV. Identification of alcohols, A., i, 455.
Reid, *Ebenezer Emmet.* See also *G. D. van* **Epps,** *Edgar M.* **Faber,** *J. W.* **Kimball,** *J. A.* **Lyman,** *Edward* **Lyons,** *John H.* **Sachs,** and *B. B.* **Wroth.**
Reid, *Edward Waymouth*, analysis of cast nichrome, A., ii, 392.
Reilly, *Joseph*, the resolution of asymmetric quinquevalent nitrogen compounds. I. The salts of *d*- and *l*-phenylbenzylmethylallylammonium hydroxide with *d*- and *l*-α-bromocamphor-π-sulphonic acid, T., 20; A., i, 129.
Reilly, *Joseph*, and *Wilfrid John* **Hickinbottom,** derivatives of *n*-butylaniline, T., 1026.
Reiman, *Clarence Kenworthy*, the absolute density of hydrogen bromide gas, A., ii, 137.
  the revision of the atomic weight of bromine; density of hydrogen bromide gas under reduced pressure, A., ii, 200.
Reinders, *Willem*, and *L.* **Hamburger,** ultra-microscopic investigation of very thin metal and salt films obtained by evaporation in high vacuum, A., ii, 405.
Reiter, *Fritz.* See *Erich* **Benary.**
Reitstötter, *Josef*, preparation of colloidal gold solutions by the nucleus method, A., ii, 481.

Reitstötter, *Josef.* See also *Richard* **Zsigmondy.**

Rengade, *Etienne*, the purification of salts by clarification or by fractional crystallisation, A., ii, 451.

Report of the Committee of the British Association on absorption spectra and chemical constitution of organic compounds, A., ii, 435.

Report of the Council, T., 273.

Repossi, *Emilo*, the crystalline form of some benzene derivatives, A., i, 549.

Resch, *Alfred*, cataphoretic investigations with thrombin and fibrinogen, A., i, 303.

Retinger, *J. M.*, the mechanism of the ninhydrin reaction; a contribution to the theory of colour of salts of alloxantin-like compounds, A., i, 519.

Reychler, *Albert*, adsorption and ionisation equilibria, A., ii, 233.

Richards, *Eric Hannaford*, dissolved oxygen in rain-water, A., i, 624.

Richards, *Theodore William*, and *Frederick Osband* **Anderegg**, inclusions in the silver voltameter, A., ii, 14.

Richards, *Theodore William*, and *Harold S.* **Davis**, improvements in calorimetric combustion, and the heat of combustion of toluene, A., ii, 237.

Richards, *Theodore William*, and *Norris Folger* **Hall**, attempt to separate the isotopic forms of lead by fractional crystallisation, A., ii, 230.

Richards, *Theodore William*, and *William Buell* **Meldrum**, the melting points of the chlorides of lithium, rubidium, and cæsium, and the freezing points of binary and ternary mixtures of these salts, including also potassium and sodium chloride, A., ii, 531.

Richards, *Theodore William*, and *Herman William* **Richter**, the absence of thermal hysteresis in the copper-constantan thermo-element between 30° and 100°, A., ii, 232.

Richards, *Theodore William*, and *Charles* **Wadsworth**, *3rd*, atomic weight of lead of radioactive origin, A., ii, 91.

Richardson, *Anna E.*, and *Helen S.* **Green**, nutrition investigations on cotton-seed meal. II., A., i, 524.
  - nutrition investigations on cotton-seed meal. III. Cotton-seed flour; the nature of its growth-promoting substances, and a study in protein minimum, A., i, 604.

Richardson, *E. A.*, and *L. T.* **Richardson**, atmospheric corrosion of commercial sheet-iron, A., ii, 175.

Richardson, *Frederic William*, estimation of free sulphuric, nitric, and picric acids in the presence of each other, A., ii, 158.

Richardson, *Leon B.*, the adsorption of carbon dioxide and ammonia by charcoal, A., ii, 526.

Richardson, *L. T.* See *E. A.* **Richardson.**

Richardson, *Owen Willans*, and *Charles Elizard* **Bazzoni**, limiting frequency in the spectra of helium, hydrogen, and mercury in the extreme ultraviolet, A., ii, 521.

Riche, *J. A.* See *John Raymond* **Murlin.**

Richet, *Charles*, lactic fermentation and thallium salts; study on heredity, A., i, 370.

Richet, *Charles*, and *Henry* **Cardot**, influence of short, slight rises in temperature on the progress of fermentation, A., i, 107.
  - a new process for the estimation of reducing substances in urine, A., ii, 556.

Richmond, *Henry Droop*, studies in steam distillation; propionic, butyric, valeric, and hexoic acids, A., i, 316.
  - studies in steam distillation; some applications of Duclaux's method, A., ii, 277.

Richmond, *Henry Droop*, and *E.* **Hembrough**, simple and efficient gas absorption apparatus, A., ii, 215.

Richmond, *Henry Droop*, and *J. E.* **Merreywether**, rapid estimation of the strength of sulphuric acid, A., ii, 503.

Richter, *G. A.* See *Hugh K.* **Moore.**

Richter, *Herman William.* See *George Shannon* **Forbes**, and *Theodore William* **Richards.**

Richter, *M. M.*, aromatic esters of sulphurous acid, A., i, 24.

Riesenfeld, *Ernst Hermann*, and *F.* **Bencker**, the action of ozone on inorganic iodine compounds, A., ii, 201.

Riesser, *Otto.* See *Alexander* **Ellinger.**

Rigotard, *Marcel*, graph for correcting volumes of gases to 0° and 760 mm., A., ii, 179.

Riiber, *Claus Nissen*, and *E.* **Berner**, resolution of the phenylglyceric acid with m. p. 122° into its optically-active components, A., i, 562.

Ringer, *Wilhelm Eduard*, significance of the condition of the substrate in the action of pepsin. III. Pekelharing's pepsin, A., i, 233.

Rinkes, *Ime Jan*, Braun's reagent, A., ii, 550.

Rinkes, *Inne Jan*, and *J. F. B. van* **Hasselt**, bixin. III., A., i, 660.

Rinne, *Fritz*, crystal stereochemistry, A., ii, 18.

the ultimate structure of crystals, A., ii, 166.

Ripper, *Maximilian*, and *Franz* **Wohack**, microanalysis of wine, A., ii, 106.

microanalysis of wine. II. Estimation of alcohol, A., ii, 512.

Rippstein, *Erwin*, the nature of mountain sickness, A., i, 428.

Ritter, *George*. See *Francis Craig* **Krauskopf**.

Ritter, *Philip A.* See *Joseph Howard* **Mathews**.

Rittmann, *Walter F.*, preparation of benzene, toluene, and other aromatic hydrocarbons from petroleum and other hydrocarbons, A., i, 14.

Ríus y Miro, *A.*, examples of electrolysis with alternating current, A., ii, 291.

Roark, *G. W.*, *jun.* See *Arthur Wayland* **Dox**.

Roark, *R. C.* See *C. C.* **McDonnell**.

Robbins, *Harold E.*, new form of conductivity cell for electro-titration, A., ii, 235.

Robert, *Adrien*. See *Friedrich* **Kehrmann**.

Robert, *T.*, the physiological significance of calcium in plants, A., i, 436.

Roberts, *W. A.* See *William Draper* **Harkins**.

Robertson, *George*. See *James Colquhoun* **Irvine**.

Robertson, *Thorburn Brailsford*, growth. VIII. Influence of a diet deficient in fats, and of the same diet with cholesterol added, on the growth of the white mouse, A., i, 65.

Robertson, *Thorburn Brailsford*, and *M.* **Delprat**, growth. IX. Influence of tethelin on the early growth of the white mouse, A., i, 673.

Robertson, *Thorburn Brailsford*, and *Carl L. A.* **Schmidt**, an electrically heated vacuum desiccator, A., ii, 28.

Robinson, (*Mrs.*) *Gertrude Maud*, azoxycatechol ethers and related substances, T., 109; A., i, 226.

Robinson, (*Mrs.*) *Gertrude Maud*, and *Robert* **Robinson**, the scission of certain substituted cyclic catechol ethers, T., 929; A., i, 692.

researches on pseudo-bases. II. Some berberine derivatives and remarks on the mechanism of the condensation reactions of pseudo-bases, T., 958; A., i, 706.

Robinson, *Robert*, a synthesis of tropinone, T., 762; A., i, 581.

a theory of the mechanism of the phytochemical synthesis of certain alkaloids, T., 876; A., i, 664.

Robinson, *Robert*. See also (*Miss*) *Janet Forrest McGillivray* **Brown**, (*Miss*) *Ellen Margaret* **Hindmarsh**, *Thomas Gilbert Henry* **Jones**, (*Miss*) *Annie Mary Bleakly* **Orr**, and (*Mrs.*) *Gertrude Maud* **Robinson**.

Robinson, *R. H.*, and *H. V.* **Tartar**, decomposition of protein substances through the action of bacteria, A., i, 498.

Rockwood, *Elbert William*, auxo-amylases, A., i, 358.

Rodd, *Ernest Harry*, the properties and constitution of some new basic salts of zirconium, T., 396; A., ii, 322.

Rodríguez Mourelo, *José*, phototropic phenomena of the sulphates of strontium, calcium, and barium, A., ii, 229.

Rodt, *Victor*, iron trisulphide and the formation of amorphous iron disulphide, A., ii, 142.

Röhlich, *B.* See *Emil* **Votoček**.

Röhmann, *Franz*, the constituents of wool fat, A., i, 78.

Roessler & Hasslacher Chemical Co., preparation of alkali percarbonates, A., ii, 412.

Roettgen, *Theodor*, estimation of lactic acid in wine by Moslinger's method, A., ii, 583.

Rogers, *Austin Flint*, rare Californian minerals, A., ii, 496.

Rohde, *Alice*, method for the identification of phenylalanine-carbamido-acid in the presence of urea and amino-acid, A., ii, 344.

Rohonyi, *Hugo*, the permeability of red blood corpuscles to electrolytes, A., i, 235.

two peculiarities of red blood corpuscles (endocoagulation and reversal of hæmolysis), A., i, 236.

Rohonyi, *Hugo*, and *A.* **Lóránt**, the action of carbon dioxide and oxygen on the permeability of red blood corpuscles to electrolytes, A., i, 235.

Rojahn, *C. A.* See *August* **Michaelis**.

Rolland. See **Thevenon.**

Rolle, *J.*, oxidimetric estimation of cuprous oxide precipitated during the analysis of sugar with Fehling's solution, A., ii, 104.

Romburgh, *Pieter van*, and *J. M. van der* **Zanden**, polymerides of methylchavicol, A., i, 690.

Rona, *Elisabeth*, rate of diffusion and diameter of the atom of radium emanation, A., ii, 286.

Rona, *Peter*. See *Herbert* **Freundlich**.

Ronnet, *L*. See *Henri* **Lajoux**.

Roon, *Leo*, and *Ralph E.* **Oesper**, theory of emulsification based on pharmaceutical practice, A., ii, 299.

Roschier, *R. H.* See *Gustav* **Komppa**.

Rose, *C. C.* See *William Ridgeley* **Orndorff**.

Rose, *Hermann*, crystallographic constants of some artificial crystals, A., ii, 257.

Rose, *Mary S.*, and *Lenna F.* **Cooper**, biological efficiency of potato nitrogen, A., i, 524.

Rose, *Robert Erstafieff*, and *Winfield* **Scott**, *jun.*, anhydroximes. II., A., i, 354.

Rosenbloom, *Jacob*, modification of Gerhardt's test for acetoacetic acid in urine, A., ii, 50.

Rosenheim, *Arthur*, and *Marianne* **Pieck**, iso- and hetero-polyacids. XIV. Heteropolyvanadates, A., ii, 212.

Rosenheim, *Arthur*, [and in part *Marianne* **Pieck**, and *Jacob* **Pinsker**], iso- and hetero-polyacids. XIII. The constitution of the polymolybdates, polytungstates, and polyvanadates, A., ii, 35.

Rosenheim, *Otto*, preparation of scyllitol from dog-fish (*Scyllium canicula*), A., i, 366.
  accessory factors for plant growth, A., i, 503.

Rosický, *Vojtěch*, the relation between density and optical refraction, A., ii, 433.

Ross, *Ellison L.* See *Hugh* **McGuigan**.

Rost, *Clayton O.*, the estimation of soil phosphorus, A., ii, 579.

Rothlin, *Ernst*. See *Adolf* **Kaufmann**.

Rothschild. See *G.* **Fenner**.

Rothschild, *S.*, estimation of nickel in the presence of zinc and iron, A., ii, 221.

Rowe, *Frederick Maurice*. See *Arthur George* **Green**.

Roy, *G.* See *H.* **Bordier**.

Royle, *Frank Albert*. See *Arthur* **Lapworth**.

Rozanov, *Nicolai Andréevitsch*, isomerisation phenomena of the three-membered ring, A., i, 84.
  isomeric transformations in the series of *cyclo*hexanol and its homologues and of *cyclo*hexylcarbinol, A., i, 132.
  spectrographic investigations of azole derivatives. I. Pyrazole and its derivatives, A., ii, 284.

Rózsa, *Michael*, the separation and thermal metamorphosis of the Zechstein salts: bischofite, kainite, and blödite, A., ii, 97.
  posthumous stratifications in "principal" anhydrite, A., ii, 214.

Rudnick, *Paul*, and *Raymond D.* **Cooke**, preparation of chloroplatinic acid by means of hydrogen peroxide, A., ii, 264.
  recovery of molybdic acid, A., ii, 320.

Rudolph, *Walter*, cantharidin. V., i, 468.

Rügheimer, *Leopold*, the relationships between keto- and enol-forms in the case in which the enolisation is caused by a positive β-influence, A., i, 335.

Ruer, *Rudolf*, and *Franz* **Goerens**, the system: iron–copper, A., ii, 474.

Ruff, *Otto*, the formation of diamonds, A., ii, 369.

Ruff, *Otto*, and *Ernst* **Jellinek**, investigations at high temperatures. X. Aluminium and carbon, A., ii, 92.

Ruff, *Otto*, and *Georg* **Lauschke**, investigations at high temperatures. IX. The preparation of articles of zirconia, A., ii, 95.

Ruff, *Otto*, *Wilhelm* **Plato**, and *Georg* **Winterfeld**, the preparation of fluorine from hydrogen fluoride or other fluorides by chemical means, A., ii, 201.

Ruff, *Otto*, and *Hans* **Rathsburg**, osmium dioxide, A., ii, 323.

Ruge. See **Zucker**.

Ruggli, *Paul*, rings containing a triple linking. III. Constitution of *cyclo*succinyldiaminotolane, A., i, 22.
  1:2- and 2:3-diphenylindene, A., i, 551.
  formation of a doubly condensed indole, A., i, 586.

Rule, *Alexander*. See *John Smeath* **Thomas**.

Runze, *P.* See *Hermann* **Thoms**.

Ruoss, *Hermann*, volumetric estimation of sugar in urine with Fehling's solution, A., ii, 549.

Ruot, *M.* See *Pierre* **Mazé**.

Rupe, *Hans*, and *E.* **Burckhardt**, β-camphorylidenepropionic acid (methylenecamphoracetic acid), A., i, 141.

Rupe, *Hans*, and *L.* **Silberstrom**, the influence of constitution on the rotation of optically active substances. IX. Absorption spectra of some compounds with "relatively abnormal" rotation-dispersion, A., ii, 435.

Rupe, *Hans*, and *W.* **Tomi**, an isomeric teresantalic acid, A., i, 138.

Rupe, *Hans*, and *Samuel* **Wild**, the influence of constitution on the rotation of optically active substances. X. Optically active ketones and diketones, A., i, 538.

Rupp, *Erwin*, constitution of hydrargyrum thymolo-aceticum, A., i, 670.
  evaluation of pyrolusite, A., ii, 390.
  estimation of bromides, A., ii, 540.

Rupp, *Erwin*, and *A.* **Herrmann**, mercuriation products of phenol-*p*-sulphonic acid, A., i, 488.
  sozoiodol-mercury compounds, A., i, 516.

Rupp, *Erwin*, and *E.* **Hollatz**, valuation of bromides, A., ii, 327.

Rushenceva, (*Mlle.*) *A. K.* See *S. S.* **Nametkin.**

Ruttan, *R. F.*, human adipocere, A., i, 495.

Ruttan, *R. F.*, and *M. J.* **Marshall**, composition of adipocere, A., i, 364.

Ryan, *Hugh*, and *W. M.* **O'Riordan**, the tinctorial constituents of some lichens which are used as dyes in Ireland, A., i, 342.

Ryan, *Hugh*, and *Phyllis* **Ryan**, condensation of aldehydes with ketones. III. Benzaldehyde with methyl *iso*propyl ketone, A., i, 348.

Ryan, *Phyllis*. See *Hugh* **Ryan.**

Ryd, *Sigfrid*, behaviour of casein toward dilute solutions of sodium chloride, A., i, 301.

Rykenboer, *Edward A.* See *Samuel Lawrence* **Bigelow.**

S.

Sabalitschka, *Th.* See *Hermann* **Thoms.**

Sabatier, *Paul*, and *Georges* **Gaudion**, the different methods of decomposition of amines by catalysis: regeneration of aniline from substituted anilines, A., i, 553.
  a new case of reversible catalysis: direct formation of nitriles from amines with the same carbon chain, A., ii, 460.

Sachanov, *Alexander N.*, electrolytic dissociation of individual salts, A., ii, 115.
  influence of electrolytes on the dissociating power of solvents. III., A., ii, 128.
  abnormal electrolytic dissociation, A., ii, 234.

Sacher, *Julius Friedrich*, a colloido-chemical phenomenon as indicator in quantitative analysis, A., ii, 180.

Sacher, *Julius Friedrich*, method for the separation of lead and iron, A., ii, 272.
  chemical evaluation of alkali chromates and dichromates, A., ii, 337.

Sachs, *A. P.*, estimation of nitrogen in nitro-compounds, A., ii, 505.

Sachs, *H.* See *R.* **Kudicke.**

Sachs, *John H.*, and *Ebenezer Emmet* **Reid**, esterfication. VII. The esterification of *o*-, *m*-, and *p*-toluic acids by ethyl mercaptan, A., i, 89.

Sage, *C. E.*, testing of acetic anhydride, A., ii, 398.

Saillard, *Emile*, [with **Wehrung**], action of acids on the rotatory power of sucrose and invert-sugar in the presence of soluble salts, A., i, 513.

St. John, *B. H.*, estimation of boric acid by titration in the presence of glycerol, A., ii, 152.

Saito, *Isaburo*. See *Masumi* **Chikashige.**

Saito, *Kendo*, chemical conditions for the development of the reproductive organs in some yeasts, A., i, 499.

Salant, *William*, and *Robert* **Bengis**, physiological and pharmacological studies on coal-tar colours. I. Fat-soluble dyes, A., i, 70.

Salant, *William*, and *Louis Elsberg* **Wise**, action of sodium citrate and its decomposition in the body, A., i, 106.

Salatko-Petrischtsche. See *Vladimir Alexandrovitsch* **Plotnikov.**

Salkover, *Benedict*, estimation of salol and acetanilide in a mixture of the two, and of salol and phenacetin in their mixtures, A., ii, 53.

Salkowski, *Ernst* [*Leopold*], the sulphur compounds of the urine, A., i, 304.
  anaesthesine and isethionyl-*p*-aminobenzoic acid, A., i, 305.
  bismuth acetate, A., i, 316.
  p-lactylaminobenzoic acid, A., i, 392.
  human gall stones, A., i, 716.
  the forerunners of Kjeldahl's method for estimating nitrogen, A., ii, 504.

Salway, *Arthur Henry*, methyl nonyl ketone from palm-kernel oil, T., 407; A., i, 438.

Samoilov, *Jakob V.*, palæophysiology: the organic origin of some minerals occurring in sedimentary rocks, A., ii, 376.
  mineralogy of phosphorite deposits. II., A., ii, 489.

Sandoz, *Maurice*. See *Friedrich* **Kehrmann.**

Sandqvist, *Håkan*, I-phenanthrene-10:3(or 6)-disulphonic acid, A., i, 552.

Sansum, *W. D.*, and *Rollin Turner* **Woodyatt**, theory of diabetes. VIII. Timed intravenous injections of dextrose at lower rates, A., i, 496.

Sasaki, *Takaoki*, biochemical changes in protein cleavage products produced by bacteria. II., A., i, 107.

Sasaki, *Y.*, comparative investigation of the behaviour of hydroaromatic substances in the animal organism, A., i, 677.

Sastry, *Sosale Garalapury*. See *William Arthur* **Haward**.

Satta, *Giuseppe*, enzymes in blood, A., i, 100.

Saunders, *William Gilbert*, obituary notice of, T., 320.

Sauvin, *Friedrich*. See *Theodor* **Curtius**.

Savings, Investments, and Trust Co., Exors., The. See *J. W.* **Aylsworth**.

Savini, *G.*, estimation of theobromine and caffeine in cacao and chocolate, A., ii, 109.

Sawyer, *H. L.* See *Claude S.* **Hudson**.

Saxton, *Blair*. See *Harry Ward* **Foote**.

Sborgi, *Umberto*, and *F.* **Mecacci**, borates: the system $Na_2O:B_2O_3:H_2O$ at 60°. III., A., ii, 138.

Scales, *F. M.*, estimation of nitric nitrogen, A., ii, 41.

Schaarschmidt, *Alfred*, anthraquinone-1-diazonium haloids, A., i, 179.

  3:4-benzofluorenone, A., i, 274.

  new method of preparing cyclic ketones, A., i, 285, 703.

Schaarschmidt, *Alfred*, [with *Eugen* **Georgeacopol**], a new benzanthrone synthesis, A., i, 274.

Schadinger, *Rudolf*. See *Robert* **Kremann**.

Schaefer, *Konrad*, [with *St.* **Deichsel**], the absorption spectrum of nitric acid vapour, A., ii, 186.

Schaefer, *Konrad*, [with *Hermann* **Niggemann**], optical investigations of the constitution of nitric acid, A., ii, 61.

  optical investigation of mixtures of nitric and sulphuric acids, A., ii, 186.

Schall, [*Joh. Friedrich*] *Carl*, anodic hydrogen peroxide formation during the electrolysis of malonates, A., ii, 118.

Schaller, *Waldemar Theodore*, identity of hamlinite with goyazite, A., ii, 177.

  composition of phosphorite minerals, A., ii, 490.

  ilsemannite, hydrous sulphate of molybdenum, A., ii, 491.

Schaller, *Waldemar Theodore*, minasragrite, a hydrous sulphate of vanadium, A., ii, 575.

Schaller, *Waldemar Theodore*. See also *G. F.* **Loughlin**.

Scharf, *W.* See *E.* **Seel**.

Scharizer, *Rudolf*, the crystal structure of the compound $H_{16}Tl_2B_{12}O_{24}$, A., ii, 473.

Scharizer, *Rudolf*, and *Julius* **Donau**, constitution and genesis of iron sulphates. IX. Voltaite from Szomolnok, Hungary, A., ii, 490.

Scharvin, *Vassili V.*, and *N. I.* **Plachuta**, action of diazo-compounds on copper acetylide; synthesis of tetraphenylethane, A., i, 179.

Scheetz, *Francis H.*, ferric oxide and alumina, A., ii, 574.

Scheffer, *Frans Eppo Cornelis*, the influence of temperature on chemical equilibria, A., ii, 170.

  allotropy of the ammonium haloids. III., A., ii, 207.

Scheffer, *Frans Eppo Cornelis*. See also *Andreas* **Smits**.

Scheibler, *Helmuth*, the chemical constituents of bituminous tar oils rich in sulphur (ichthyol oils). II., A., i, 153.

Scheidler, *H.*, use of hydrazine sulphate and potassium bromide in the estimation of sulphides in ores, A., ii, 503.

Schelenz, *Hermann*, when did the alchemists Jan Isaac of Holland and Isaac of Holland live? A., ii, 529.

Scheminzký, *F.*, photographic detection of emanations in biological processes, A., i, 73.

Scherrer, *J. A.* See *Russel S.* **McBride**.

Scherrer, *P.* See *Peter* **Debye**.

Schicht, *G.*, and *Adolf* **Grün**, preparation of ketones, A., i, 443.

Schimank, *H.* See *J.* **Eggert**.

Schindhelm, *Hans*. See *Ludwig* **Gattermann**.

Schjelderup, *H.* See *L.* **Vegard**.

Schläpfer, *Victor*, localisation of the processes of oxidation in the cell and the modifications induced by combinations of electrolytes, A., i, 187.

Schlenk, *Wilhelm*, and *Johanna* **Holtz**, the simplest organo-metallic alkali compounds, A., i, 255.

  benzyltetramethylammonium, A., i, 262.

  ammonium compounds of a new type, A., i, 262.

Schlundt, *Herman*. See *Albert G.* **Loomis**.

Schmerda, condensation product of ammonium thiocyanate with formaldehyde, A., i, 545.
Schmid, *Max*. See *Fritz* **Fichter**.
Schmidt, *Albert*, a simple exponential function for the representation of several physico-chemical phenomena; vapour tension of liquids and solids, dissociation pressure, equilibrium constants, densities of liquids and vapours, and radiation from black bodies, A., ii, 406.
Schmidt, *Carl L. A.* See *Thorburn Brailsford* **Robertson**.
Schmidt, *Ernst*, scopoline bromide, A., i, 409.
  formation of guanidine from thiocarbamide and from cyanamide, A., i, 449.
  desulphurisation of thiocarbamides (formation of carbamide), A., i, 687.
  formation of carbamide from cyanamide, A., i, 688.
  arsenic trisulphide, A., ii, 331.
Schmidt, *L.*, preparation of protocatechualdehyde, A., i, 272.
Schmidt, *R.* See *W.* **Appelius**.
Schmitz, *K. H.*, preparation of salts of hexamethylenetetraminemethyl hydroxide, A., i, 324.
Schneck, *Hermann*. See *Wilhelm* **Wislicenus**.
Schneider, *A.* See *Charles* **Dhéré**.
Schneider, *Wilhelm*, and *Fritz* **Wrede**, synthesis of disaccharides containing sulphur and selenium, A., i, 540.
Schnorr, *Walter*, the dissolution of sodium chloride crystals in solutions containing carbamide, A., ii, 469.
Schoch, *Eugene Paul*, and *R. H.* **Pritchett**, the electrolytic preparation of hydroxylamine hydrochloride, A., ii, 29.
Schoeller, *Walter*. See *Walther* **Schrauth**.
Schoeller, *Walter R.*, and *A. R.* **Powell**, rapid method for estimating nickel and cobalt in ores and alloys. I., A., ii, 425.
Schöllköpf, *Karl*. See *Wilhelm* **Wislicenus**.
Schoenflies, *A.*, crystal structure. I. and II., A., ii, 447.
Schoepfle, *C. S.* See *Moses* **Gomberg**.
Schöttle, *Iv.*, inactivity of the γ-carbonyl of certain pyrone and pyridone derivatives, A., i, 166.
Schollenberger, *Charles J.*, relation between indications of several lime-requirement methods and the soil's content of bases, A., i, 440.
  [estimation of the] total carbon in soil by wet combustion A., ii, 103.
Scholten, *B. G. B.* See *Walther* **Borsche**.
Scholtz, *Max*, action of γ-diketones on unsaturated ketones, A., i, 462.
Scholz, *H. A.*, and *P. J.* **Waldstein**, a rapid method for the estimation of water-soluble arsenic in lead arsenate, A., ii, 422.
Schoorl, *Nicolaas*, and *I. M.* **Kolthoff**, estimation of sugar, A., ii, 514.
Schoorl, *Nicolaas*, and (*Mej.*) *A.* **Regenbogen**, quantitative estimation of sugar, A., ii, 222.
Schorger, *A. W.*, the oleoresin of Douglas fir, A., i, 467.
Schott, *J. E.* See *Fred W.* **Upson**.
Schrader, *Ernst*, picryl azide, A., i, 595.
  hydrazides and azides of sulphocarboxylic acids. I. Action of hydrazine on ethyl *o*-aminosulphonylbenzoate, A., i, 709.
Schramm, *W. H.* See *Friedrich* **Mayer**.
Schrauth, *Walther*, and *Walter* **Schoeller**, disinfecting power of complex organic mercury compounds. III. Mercuriated phenols, A., i, 241.
Schreinemakers, *Frans Antoon Hubert*, non-, uni- and bi-variant equilibria, A., ii, 132, 169, 195, 247, 299, 411, 454.
Schreinemakers, *Frans Antoon Hubert*, and (*Miss*) *Woutrine Constance de* **Baat**, combinations of arsenious anhydride and salts. I., II., and III., A., ii, 173, 203.
  sodium arsenites, A., ii, 206.
Schroeder, *J. P.*, an automatic suction attachment for an ordinary pipette, A., ii, 418.
Schroeter, *Georg*, [with *Hans* **Kesseler**, *Otto* **Liesche**, and *R. F.* **Müller**], the relationships of the polymeric ketens to *cyclo*butane-1:3-dione and its derivatives, A., i, 145.
Schryver, *Samuel Barnett*, and (*Miss*) *Dorothy* **Haynes**, pectic substances of plants, A., i, 245.
Schryver, *Samuel Barnett*, and *Mary* **Hewlett**, the phenomena of "clot" formation. IV. The diphasic erosive action of salts on the cholate gel, A., ii, 22.
Schryver, *Samuel Barnett*. See also *Albert Theodore* **King**.
Schubart. See *Max* **Bodenstein**.
Schubnikov, *A.*, the influence of temperature variations on the formation of crystals, A., ii, 449.
  the relation between rate of growth and external symmetry of crystals, A., ii, 450.

Schürmann, *Grete*. See *Theodor* **Zincke**.

Schulemann, *Werner*, vital stains, A., i, 369, 612.
  intra vitam staining with acid dyes and its significance for anatomy, physiology, pathology, and pharmacology, A., i, 429.
  considerations relative to the intra vitam staining with acid dyes, A., i, 429.

Schultz, *M. P.* See *Victor* **Lenher**.

Schulz, *Ferd.*, the optical isomerism of the abietic acids, A., i, 649.

Schulz, *Fr.* See *Alexander* **Gutbier**.

Schulze, *Heinrich*, and *A.* **Liebner**, aconite alkaloids; pyraconitine and pyraconine, A., i, 470.

Schumacher, *G.*, estimation of chromium in ferrochrome, A., ii, 337.

Schumm, *Otto*, [porphyrins] valuation of spectroscopic methods, A., i, 712.
  amount of dextrose in blood, A., i, 713.
  hæmatoporphyria congenita and the natural porphyrins, A., i, 715.

Schumoff-Deleano, *Vera*, synthetical experiments in the pyroxene group, A., ii, 496.

Schuppli, *O.* See *W. I.* **Baragiola**.

Schwartz, *E. H.* See *R. C.* **Haff**.

Schwarz, *Robert*, ammonium silicate, A., ii, 31.

Schweiger, *J.* See *Rudolf Friedrich* **Weinland**.

Schweitzer, *Karl*, deamidisation, A., i, 504.

Scott, *Alexander*, presidential address, T., 288.

Scott, *Leonard C.*, and *Rollin G.* **Myers**, the use of potassium persulphate in the estimation of total nitrogen in urine, A., ii, 380.

Scott, *R. W.*, *T. W.* **Thoburn**, and *Paul J.* **Hanzlik**, the salicylates. IV. Salicylate in the blood and joint fluid of individuals receiving full therapeutic doses of the drug, A., i, 241.

Scott, *R. W.* See also *John James Rickard* **Macleod**.

Scott, *Sewell E.* See *Percy Embury* **Browning**.

Scott, *Winfield, jun.* See *Robert Evstafieff* **Rose**.

Sears, *George W.*, tantalum chloride with reference to its use in the determination of the atomic weight of tantalum, A., ii, 481.

Sedgwick, *J. P.* See *F. B.* **Kingsbury**.

Seel, *E.*, and *C.* **Kelber**, molecular weight of aloin and its products of oxidation, A., i, 41.

Seel, *E.*, *C.* **Kelber**, and *W.* **Scharf**, products of oxidation of aloin, A., i, 577.

Seibert, *Frank M.*, *George Augustus* **Hulett**, and *Hugh Stott* **Taylor**, standard cells and the Nernst heat theorem, A., ii, 231.

Seidell, *Atherton*, vitamine content of brewers' yeast, A., i, 362.

Seidenberg, *Armin*, method for fractionating fats and oils, A., i, 626.

Seligman, *Richard*, aluminium production by electrolysis; the mechanism of the reaction, A., ii, 414.

Seligman, *Richard*, and *P.* **Williams**, the action of acetic acid on aluminium, A., ii, 317.

Sem, *M.*, constitution of manganic compounds, A., ii, 319.

Semple, *C. C.*, estimation of phosphoric acid in phosphate rock, A., ii, 505.

Sen, *Jnanendra Nath.* See *Rasik Lal* **Datta**, and *Prafulla Chandra* **Mitter**.

Sen, *Surya Narayan.* See *Barun Chandra* **Dutt**.

Senft, *Emanuel*, anatomy and chemism of the lichen, *Chrysothrix nolitangere*, A., i, 506.

Senior, *James Kuhn*, the molecular rearrangement of triarylmethylazides, A., i, 97.

Senior, *James Kuhn.* See also *Julius* **Stieglitz**.

Senter, *George*, and *Gerald Hargrave* **Martin**, studies on the Walden inversion. V. The kinetics and dissociation constant of α-bromo-β-phenylpropionic acid, T., 447; A., ii, 301.

Serex, *Paul, jun.*, plant food materials in the leaves of forest trees, A., i, 505.

Seufert, *Rud.* See *Max* **Busch**.

Seuffert, *Rudolf W.* See *Max* **Cremer**.

Seyler, *Clarence Arthur*, and *Percy Vivian* **Lloyd**, studies of the carbonates. II. Hydrolysis of sodium carbonate and sodium hydrogen carbonate and the ionisation constants of carbonic acid, T., 138; A., ii, 196.
  studies of the carbonates. III. Lithium, calcium, and magnesium carbonates, T., 994; A., ii, 571.

Sharpe, *John Smith*, preparation of guanidine, A., i, 121.
  distribution of nitrogen in beer, A., i, 620.
  rapid process for the estimation of the higher fatty acids and soaps in fæces, A., ii, 516.

Sharpe, *John Smith.* See also *J. H.* **Paul**.

Shaw, *Jos. A.*, filter flask, A., ii, 499.

Shaw, *William M.* See *Ross Aiken* **Gortner.**
Shedlov, *A.* See *J. F.* **McClendon.**
Sheib, *S. H.* See *J. T.* **Leary.**
Shemtschushni, *Sergius F.*, alloys of certain haloid salts of silver and of alkali metals, A., ii, 140.
Shepard, *Norman A.*, amines. VI. The utilisation of hypochlorite colour reactions in establishing the mechanism of the action of methyl sulphate on aniline, A., i, 19.
Sheppard, *Samuel Edward*, measurement of the absolute viscosity of very viscous media, A., ii, 359.
Sherman, *Henry Clapp*, and *Dora E.* **Neun**, certain methods for the study of proteolytic action, A., ii, 111.
Sherman, *Henry Clapp*, and *Jennie A.* **Walker**, influence of certain electrolytes on the course of the hydrolysis of starch by malt amylase, A., i, 597.
Sherwin, *Carl P.*, comparative metabolism of certain aromatic acids, A., i, 603.
Sherwin, *Carl P.* See also *Carl* **Voegtlin.**
Sherwood, *C. M.* See *Emile Monnin* **Chamot.**
Shibata, *Keisaku*, *I.* **Nagai**, and *M.* **Kishida**, occurrence and physiological significance of flavone derivatives in plants, A., i, 107.
Shibata, *Yuji*, [with *K.* **Matsuno**], researches on the absorption spectra of metal ammines. II. (*a*) Absorption spectra and electrolytic conductivity of aqueous solutions of co-ordination polymeric nitroammine-cobalt complexes; (*b*) absorption spectra of aqueous solutions of polynuclear ammine-cobalt complexes, A., ii, 186.
Shipper, *Vernon C.*, pure sodium chloride, A., ii, 571.
Shorey, *Edmund C.*, and *Wm. H.* **Fry**, the influence of calcite inclusions on the estimation of organic carbon in soils, A., ii, 422.
Shorey, *Edmund C.* See also *R. F.* **Gardiner.**
Shoub, *H. L.* See *Earle Bernhard* **Phelps.**
Shuey, *Philip McG.*, the volumetric or Pemberton method for estimating phosphoric acid, with some experiments showing the influence of temperature and the sulphuric acid radicle on the results, A., ii, 269.
Sidersky, *D.*, estimation of sugar in urine, A., ii, 548.
Sieburg, *Ernst*, esters of aromatic arsenic compounds (*p*-benzarsinic acid) and amino-acids and higher alcohols, A., i, 486.
Siegbahn, *Manne*, spectra of high frequency, A., ii, 402.
Siegbahn, *Manne*, and *W.* **Stenström**, the X-ray spectra of isotopic elements, A., ii, 524.
Sieger, *H.* See *Alfred* **Heiduschka.**
Sievers, *Arthur F.*, the caoutchouc from *Eucommia ulmoides*, Oliver, A., i, 346.
Sieverts, *Adolf*, and *Rich.* **Brandt**, apparatus for the estimation of rare gases (argon), A., ii, 103.
Silbermann, *S.*, the law of the periodicity of the elements, and the natural periodic system, A., ii, 27.
Silberstein, *Fritz.* See *Karl* **Baldes.**
Silberstein, *L.*, dispersion and the size of molecules of hydrogen, oxygen, and nitrogen, A., ii, 161.
Silberstrom, *L.* See *Hans* **Rupe.**
Sill, *Herbert Fowler*, influence of pressure on solubility, A., ii, 75.
Simek, *Ant.* See *B.* **Ježek.**
Simmonds, *Nina.* See *Elmer Verner* **McCollum.**
Simonis, *Hugo*, the hydrolysis of chromones by dilute alkali, A., i, 580.
  periodides in the coumarin series, A., i, 705.
Simonis, *Hugo*, and *L.* **Herovici**, bromine substitution products of chromones [benzopyrones], A., i, 408.
  2:3:5:7-tetramethylchromone, A., i, 580.
Simonsen, *John Lionel*, and *Madyar Gopala* **Rau**, nitration of isomeric acetylaminomethoxybenzoic acids, T., 220; A., i, 336.
Simonsen, *John Lionel.* See also *Charles Stanley* **Gibson.**
Simpson, *Edward Sydney*, tapiolite from Western Australia, A., ii, 377.
Simpson, *Edward Sydney*, and *Maurice A.* **Brown**, natrojarosite from Kundip, Western Australia, A., ii, 146.
Sinks, *F. L.* See *William Lloyd* **Evans.**
Sisley, *Paul*, the solvent properties of emulsions; theory of dyeing in a "boiled off liquor" bath, A., ii, 527.
Sjöström, *F. W.*, volumetric estimation of zinc in zinc chloride, nitrate and sulphate, A., ii, 153.
  zinc perhydrates; [hydroperoxides], A., ii, 533.
Skarnitzl, *E.* See *František* **Slavík.**
Skirrow, *Frederick William.* See *W. H.* **Hatcher.**
Skrabal, *Anton*, fusion diagram of the system, methyl oxalate–water, A., i, 317.
  a compound of ethyl oxalate with potassium tri-iodide, A., i, 378.

Skrabal, *Anton*, consecutive reactions. II. Kinetics of the hydrolysis of the methyl esters of oxalic acid, A., ii, 250.

Skrabal, *Anton*, and *Josef* **Gruber**, alkali double fluorides of quadrivalent elements, A., ii, 263.

Skraup, *Siegfried*, vital stains, A., i, 369.

Skraup, *Siegfried*. See also *Eduard* **Buchner**.

Slavík, *František*, *E.* **Skarnitzl**, *K.* **Preis**, and *A.* **Jílek**, new phosphates from Greifenstein, Saxony, A., ii, 145.

Slyke, *Donald D. van*, estimation of amino-nitrogen in urines containing dextrose and albumin, A., ii, 41.
  gravimetric estimation of β-hydroxybutyric acid, A., ii, 107.
  estimation of oxygen in blood, A., ii, 328.
  acidosis. II. Estimation of carbon dioxide and carbonates in solution, A., ii, 422.

Slyke, *Donald D. van*, and *Glenn E.* **Cullen**, mode of action of urease and of enzymes in general, A., i, 182.
  acidosis. I. Concentration of hydrogen carbonate in the blood plasma; its significance, and its estimation as a measure of acidosis, A., i, 521.

Slyke, *Donald D. van*, *Edgar* **Stillman**, and *Glenn E.* **Cullen**, acidosis. V. Alveolar carbon dioxide and plasma hydrogen carbonate in normal men during digestive rest and activity, A., i, 523.

Slyke, *Donald D. van*. See also *Reginald* **Fitz**, and *Edgar* **Stillman**.

Smalley, *Oliver*, influence of arsenic in brass, A., ii, 315.

Smith, *C. M.* See *C. C.* **McDonnell**.

Smith, *Donald Pritchard*, and *Frederick H.* **Martin**, occlusion of hydrogen by a palladium cathode, A., ii, 64.

Smith, *George McPhail*, contamination of precipitates in gravimetric analysis; solid solution and adsorption versus higher order compounds, A., ii, 371.

Smith, *George McPhail*, and *T. R.* **Ball**, heterogeneous equilibria between aqueous and metallic solutions. III. The interaction of mixed salt solutions and liquid amalgams; a study of the ionisation relations of sodium and potassium chlorides and sulphates in mixtures, A., ii, 247.

Smith, *George McPhail*, and *S. A.* **Braley**, heterogeneous equilibria between aqueous and metallic solutions; the interaction of mixed salt solutions and liquid amalgams. IV. The ionisation relations of sodium and strontium chlorides in mixtures, A., ii, 455.

Smith, *John Henry*, new acid sodium phosphate and its action on glass, porcelain, silica, platinum, and nickel vessels, A., ii, 309.
  constitution of the alkali phosphates and some new double phosphates, A., ii, 309.
  estimation of phosphoric acid and phosphates by alkalimetric methods, A., ii, 330.

Smith, *L.*, use of diphenylamine and diphenylbenzidine for colorimetric estimations, A., ii, 217.

Smith, *L. Millard*, and *Howard B.* **Lewis**, the normal metabolism of the guinea-pig, A., i, 714.

Smith, *O. C.*, estimate of phosphoric acid after citrate digestion, A., ii, 100.

Smith, *O. C.*, and *D. G.* **Morgan**, simple mercury-sealed ether still, A., ii, 28.

Smith, *Sydney W.*, surface tension and cohesion in metals and alloys, A., ii, 408.

Smith, *William B.*, estimation of sugar in meat products, particularly extracts, A., ii, 49.

Smits, *Andreas*, an improved ebullioscope, A., ii, 66.
  influence of the solvent on the situation of the homogeneous equilibrium, A., ii, 171.
  the system-mercury iodide, A., ii, 174.

Smits, *Andreas*, and *Adriaan Hendrik Willem* **Aten**, the application of the theory of allotropy to electromotive equilibria. III. Consideration of the solubility of metal and electrons, A., ii, 232.

Smits, *Andreas*, and *S. C.* **Bokhorst**, the system phosphorus in light of the theory of allotropy, A., ii, 30.

Smits, *Andreas*, and *Cornelis Adriaan Lobry de* **Bruyn**, a new method for the passification of iron, A., ii, 262.

Smits, *Andreas*, and *Frans Eppo Cornelis* **Scheffer**, the interpretation of the Röntgenograms and Röntgen spectra of crystals, A., ii, 78.

Smoluchowski, *M. von*, mathematical theory of the kinetics of the coagulation of colloidal solutions, A., ii, 297.

Smyth, *F. Hastings*, sodium-lead compounds in liquid ammonia solution, A., ii, 473.

Sneed, *M. Cannon*. See *Lauder William* **Jones**.

Snyder, *R. S.* See *Ralph S.* **Potter**.

Société Chimique des Usines du Rhône, preparation of chloro-derivatives of organic substances, A., i, 15.

Société pour l'Industrie Chimique à Bâle, electrolytic preparation of aromatic amino-hydroxy-compounds, A., i, 197.
  silver compound of the acridine series (disinfectant), and a process of making the same, A., i, 582.
  cadmium compounds of the acridine series, and a process of making the same, A., i, 582.
  preparation of compounds of alkaloids of the morphine group, A., i, 664.
  highly active vitamine preparation thoroughly freed from inactive ingredients, A., i, 664.

Soddy, *Frederick*, separation of isotopes, A., ii, 437.

Söderbaum, *Henrik Gustaf*, the characteristic effect of ammonium salts on plant physiology, A., i, 192.

Soenderop, *Helene*. See *Erich* **Benary.**

Sörensen, *Sören Peter Lauritz*, the synthesis of amino-acids; allylhippuric acid, A., i, 89.

Sokolov, *A. M.*, molecular destruction of kaolinite by heat, A., ii, 492.

Solvay Process Co., preparation of chlorine gas, A., ii, 530.

Sommer, *Fritz*, the "supposed" importance of nitrous acid in the formation of hydrazoic acid by the oxidation of hydrazine, A., ii, 30.

Somogyi, *R.*, surface-tension tables from data by Traube and Forch, A., ii, 124.

Sonn, *Adolf*, lichen products. II. Synthesis of rhizonic acid, A., i, 143.
  preparation of benzylidene compounds of ethyl 4:5:7-trihydroxycoumarin-8(or 6)-carboxylate, A., i, 277.

Soós, *Aladar von*. See *Dionys* **Fuchs.**

Sorge, *Hermann*. See *Heinrich* **Wieland.**

Sosman, *Robert B.*, some problems of the oxides of iron, A., ii, 175.

Spaans, *Walter*. See *Samuel Mansfield* **Jones.**

Spallart, *Karl Neumann R. von*, apparatus for the extraction of sulphur from arsenic trisulphide precipitates, A., ii, 102.

Spar Chemical Co., separation of sodium and potassium salts, A., ii, 87.

Speitel, *René*. See *Friedrich* **Kehrmann.**

Spek, *Jac. van der*. See *Hugo Rudolph* **Kruyt.**

Spencer, *S. O.* See *L. H.* **Duschak.**

Spengel, *A.* See *Emil* **Ramann.**

Sperlich, *Adolf*, iodine as a useful microchemical reagent for tannin, especially as regards the distribution of tannin and starch in vegetable tissues, A., ii, 400.

Spero, *Samuel*. See *Joseph Howard* **Mathews.**

Speyer, *Edmund*. See *Martin* **Freund.**

Spica, *Carlo Luigi*, detection of mercury for forensic purposes, A., ii, 543.

Spiegel, *Leopold* [*Julius*], double bond and the electron theory, A., ii, 28.

Spielmann, *Percy E.*, and *F. B.* **Jones,** estimation of xylene in solvent naphtha, A., ii, 339.

Spitzer, *George*. See *R. H.* **Carr.**

Splawa-Neyman, *Hans von*. See *Carl Dietrich* **Harries.**

Springer, *J. W.*, volumetric estimation of zinc, A., ii, 509.

Stackmann, *L.* See *Walther* **Borsche.**

Stadnikov, *George L.*, purification of vegetable fibres, A., i, 119.
  reaction of esters with organo-magnesium compounds. IV., A., i, 136.

Stähler, *Arthur*, reactions under high pressures. IV. Synthesis of cyanides in the electric autoclave, A., i, 13.

Stähler, *Arthur*, and *Bruno* **Tesch,** new determination of the atomic weight of tellurium, A., ii, 202.

Stagner, *Bert Allen*, the molecular rearrangement of triarylmethylhydroxylamines, A., i, 23.

Stagner, *Bert Allen*. See also *Julius* **Stieglitz.**

Stahrfoss, *Knut*. See *Friedrich* **Kehrmann.**

Staněk, *Vladimir*, the nitrogenous pigments of molasses, A., i, 381.
  the origin of the nitrogenous pigments in sugar refinery products, A., i, 544.
  the nitrogenous pigments of molasses, A., i, 545.
  influence of amino-acids and of *l*-glutiminic acid in the estimation of raffinose and sucrose in molasses by the inversion method, A., ii, 342.

Stanescu, *C.* See *Charles Eugène* **Guye.**

Stanford, *Robert Viner*. See *Carl Dietrich* **Harries.**

Stansbie, *John Henry*, the analysis of some aluminium alloys, A., ii, 510.

Stansfield, *J.*, retarded diffusion and rhythmic precipitation, A., ii, 125.

Stapenhorst, *J.*, [the passive condition of metals], A., ii, 290.

Stark, *Johannes*, determination of the spectrum of a univalent polyatomic ion, and in particular of the $H^{\cdot}_2$ ion, A., ii, 281.
  the emission of a continuous spectrum in the combination of an electron with a positive ion, A., ii, 281.

Staronka, *Wilhelm*. See *Jan von* **Zawidzki.**

Staudinger, *Hermann*, and *H.* **Becker**, ketens. XXVI. Ketenmonocarboxylic esters, A., i, 629.

Staudinger, *Hermann*, and *R.* **Endle**, *p*-dimethylaminobenzoyl chloride, A., i, 646.
  ketens. XXIX. Comparison of carbimides with ketens, A., i, 666.

Staudinger, *Hermann*, [with *R.* **Endle**, *J.* **Modrzejewski**, and *H.* **Hirzel**], ketens. XXVIII. Ketencarboxylic esters and Schiff's bases, A., i, 650.

Staudinger, *Hermann*, and *H.* **Hirzel**, diazo-compounds. XIV. Decomposition of derivatives of ethyl diazoacetate by heat, A., i, 178.
  ketens. XXVII. Ethyl ketendicarboxylate and methyl phenylketencarboxylate, A., i, 630.

Stearns, *Orlo*, distilling head, A., ii, 567.

Steenbergen, *H. D.*, sulphuric acid for [use in] the nitrate test, A., ii, 421.
  estimation of salicylic acid in foods, A., ii, 549.

Steenbock, *H.*, isolation of stachydrin from lucerne hay, A., i, 439.

Steffenhagen. See **Potjan.**

Stefl, *Anton*, crystallographic investigations of the succinic acids, their homologues and derivatives, A., i, 535.

Stehle, *Raymond L.*, effect of hydrochloric acid on the mineral excretion of dogs, A., i, 609.

Steiger, *George*. See *Esper Signius* **Larsen.**

Steinkopf, *Wilhelm*, thiophen series. IX. New method of preparation of thienyl ketones, A., i, 278.

Steinkopf, *Wilhelm*, [with *Martin* **Bauermeister**], thiophen series. VII. Thiophen compounds containing mercury or arsenic, A., i, 302.

Steinkopf, *Wilhelm*, and *Dora* **Jaffé**, thiophen series. VIII. Some derivatives of 2-acetothienone, A., i, 277.

Steinmetz, *Hermann*, crystallographic investigation of some nitro-derivatives of benzene, A., i, 548.
  the crystalline form of *a*-naphthol, A., i, 557.
  the crystalline form of maltol (lariscinic acid, 3-hydroxy-2-methyl-1:4-pyrone), A., i, 580.

Stemmer, *Johann*. See *Martin* **Freund.**

Stenström, *W.* See *Manne* **Siegbahn.**

Stewart, *Alfred Walter*, and *Robert* **Wright**, solvent effect and Beer's law, T., 183; A., ii, 186.

Stewart, *Alfred Walter*. See also *Alexander Killen* **Macbeth**, and (*Miss*) *Elizabeth* **MacDougall.**

Steyer, *Hermann*. See *Carl* **Paal.**

Stieger, *Karl H.*, rhodanines, parabanic acids, and related substances, A., i, 171.

Stieglitz, *Julius*, and *James Kuhn* **Senior**, the molecular rearrangement of *sym*-bistriarylmethylhydrazines, A., i, 97.

Stieglitz, *Julius*, and *Bert Allen* **Stagner**, molecular rearrangements of β-triphenylmethyl-β-methylhydroxylamines and the theory of molecular rearrangement, A., i, 22.

Stiles, *Walter*, and *Ingvar* **Jörgensen**, permeability. IV. The action of various organic substances on the permeability of the plant cell, and its bearing on Czapek's theory of the plasma membrane, A., i, 435.

Still, *Charles James*. See *Henry* **Wren.**

Stillman, *Edgar*, *Donald D. van* **Slyke**, *Glenn E.* **Cullen**, and *Reginald* **Fitz**, acidosis. VI. Blood, urine, and alveolar air in diabetic acidosis, A., i, 523.

Stillman, *Edgar*. See also *Donald D. van* **Slyke.**

Stock, *Alfred*, determination of melting-points at low temperatures, A., ii, 192.
  nomenclature of silicon compounds, A., ii, 204.
  silicon chemistry and carbon chemistry, A., ii, 204.
  experimental manipulation; the manipulation of small quantities of volatile substances. II., A., ii, 442.

Stock, *Alfred*, and *Ernst* **Kuss**, carbon oxysulphide, COS, A., ii, 205.

Stock, *Alfred*, and *Hugo* **Stoltzenberg**, preparation of carbon suboxide from malonic acid and phosphoric oxide, A., ii, 308.

Stoddart, *Frederick Wallis*, obituary notice of, T., 376.

Stoermer, *Richard*, *F.* **Grimm**, and *E.* **Laage**, β-alkylated cinnamic acids and their stereoisomerides, A., i, 647.

Stoermer, *Richard*, and *E.* **Laage**, alkylated indones, A., i, 654.

Stoklasa, *Julius*, the physiological significance of potassium in plants, A., i, 682.

Stollé, *Robert*, preparation of 2:3-diketodihydrothionaphthens, A., i, 91.

Stoltzenberg, *Hugo*, the pigments of molasses and de-saccharification residues. II., A., i, 153.

Stoltzenberg, *Hugo*. See also *Alfred* **Stock.**

Stortenbeker, *W.*, the crystalline forms of the two naphthols, A., i, 557.

Strachov, *N. P.*, inner mechanism of the reaction of the photochemical oxidation of hydrogen iodide, A., ii, 113.

Strassner, *H.* See *Walter* **Griesbach.**

Straub, *Walther*, the development of the typical glucosides of the leaf in germinating and growing digitalis plants, A., i, 615.

Stremme, *Hermann*, transformation of the sesquioxides in woodland soils; (formation of ortstein and laterite), A., i, 512.

Strufe, *Karl.* See *Heinrich* **Biltz.**

Strutt, (*Hon.*) *Robert John*, spectroscopic observations on the active modification of nitrogen. V., A., ii, 282.

Strutt, (*Hon.*) *Robert John.* See also *Alfred* **Fowler.**

Stuber, *B.*, and *R.* **Heim**, the coagulation of the blood. I. and II., A., i, 100.

Stuber, *B.*, and *Fr.* **Partsch**, the coagulation of the blood. III., A., i, 101.

Stuckardt, *Karl.* See *Alfred* **Coehn.**

Stutterheim, *G. A.*, estimation of formalin, A., ii, 430.

Stutzer, *Albert*, the biochemistry of plants, A., i, 439.

estimation of dicyanodiamide in nitrolime, A., ii, 159.

Suarez, *M. L.*, an isomeride of glycuronic acid, A., i, 249.

Suárez, *P.*, maize diet and its connexion with pellagra, A., i, 69.

Sucharda, *Ed.* See *Stefan von* **Niementowski.**

Sudborough, *John Joseph*, additive compounds of trinitrobenzene, A., i, 84.

Sudborough, *John Joseph*, and *Jamiat Vishindas* **Lakhumalani**, the displacement of sulphonic acid groups in aminosulphonic acids by halogen atoms, T., 41; A., i, 128.

Sudborough, *John Joseph.* See also *Shunker Trimbak* **Cadre.**

Sugiura, *Kanematsu*, and *Kaufman George* **Falk**, bromine and iodine compounds of hexamethylenetetramine (urotropine), A., ii, 54.

Sullivan, *Michael Xavier*, lignoceric acid from rotten oak wood, A., i, 8.

Sure, *Barnett*, and *Edwin Bret* **Hart**, effect of temperature on the reaction of lysine with nitrous acid, A., ii, 551.

Sure, *Barnett.* See also *Edwin Bret* **Hart.**

Svanberg, *Olof.* See *Hans von* **Euler.**

Svedberg, *Theodor*, chemical reactions in anisotropic liquids. III and IV., A., ii, 249, 439.

Swann, *H.*, estimation of sodium sulphide in sulphide dye-baths, A., ii, 385.

Swanson, *C. O.*, and *E. L.* **Tague**, nitrogen in amino-form as estimated by formaldehyde-titration in relation to some other factors measuring quality in wheat flour, A., ii, 276.

Sweeney, *Orland R.*, analysis of certain tungsten derivatives, A., ii, 45.

an improved hydrogen chloride generator, A., ii, 568.

Sweeney, *Orland R.*, *Harry E.* **Outcault**, and *James R.* **Withrow**, estimation of sulphur dioxide [in gases and air], A., ii, 577.

Sweeney, *Orland R.*, and *James R.* **Withrow**, the chemical examination of natural brines, A., ii, 423.

Sweet, *Joshua Edwin.* See *John Raymond* **Murlin**, and *Alonzo Englebert* **Taylor.**

Sykora, *J.* See *E.* **Truog.**

Synthetic Hydro-Carbon Co., treatment of xylene and other aromatic hydrocarbons to obtain lower hydrocarbons of the same series, A., i, 15.

Synthetic Patents Co., preparation of pharmaceutical products containing arsenic, A., i, 196.

condensation product of cholic acid with formaldehyde, A., i, 318.

Szyszkowski, *Bohdan de*, the actual state of the theory of electrolytic dissociation in water and non-aqueous solvents, A., ii, 127.

T.

Tacconi, *Emilio*, the limestones and calciphyres of Candoglia, Italy, A., ii, 495.

artificial iron-rhodonite in slags from Elba, Italy, A., ii, 497.

Taege, *E.* See *Friedrich* **Krüger.**

Tagliavini, *Achille*, volumetric estimation of mercuric oxycyanide, A., ii, 510.

Tague, *E. L.* See *C. O.* **Swanson.**

Taigner, *E.* See *Josef* **Herzig.**

Takamine, *Toshio*, and *Shigeharu* **Nitta**, the spark and the vacuum arc spectra of some metals in the extreme ultraviolet, A., ii, 402.

Takamine, *Toshio*, and *Usaburo* **Yoshida**, the effect of an electric field on the spectrum lines of hydrogen, A., ii, 401.

Tammann, *Gustav* [*Heinrich Johann Apollon*], the melting-points of homologous series, A., ii, 441.

resistance limits of mixed crystals and the molecular arrangement in space lattices, A., ii, 448.

a colourless modification of mercuric iodide, A., ii, 474.

Tancov, *N. V.*, intermediate compounds in the hydrolysis of fats by the lipase of *Ricinus* seeds, A., i, 182.

direction of spontaneous transformations, A., ii, 367.

Tanzen, *Heinrich*, evaluation of podophyllin, A., ii, 400.

Tartar, *H. V.* See *R. H.* **Robinson.**

Taylor, *Alonzo Englebert*, *C. W.* **Miller**, and *Joshua Edwin* **Sweet**, Bence-Jones proteinuria. II., A., i, 368.

Taylor, *Hugh Stott*, thermodynamic properties of silver and lead iodides, A., ii, 14.

Taylor, *Hugh Stott*, and *Harold Wilberforce* **Close**, the catalytic influence of acids in lactone formation. I. Valerolactone, A., ii, 253.

Taylor, *Hugh Stott*. See also *William Roland* **Henderson**, and *Frank M.* **Seibert.**

Taylor, *John*, constitution of the salts of *S*-alkylthiocarbamides, T., 650; A., i, 514.

Taylor, *John*. See also *Augustus Edward* **Dixon.**

Taylor, *Joseph*. See *Harold Cornelius* **Bradley.**

Taylor, *W. A.*, and *Solomon Farley* **Acree**, measurement of the electrical conductivity of solutions at different frequencies. V. Investigations on the use of the Vreeland oscillator and other sources of current for conductivity measurements, A., ii, 7.

measurement of the electrical conductivity of solutions at different frequencies. VI. Investigations on bridge methods, resistances, cells, capacities, inductances, phase relations, precision of measurements, and a comparison of the resistances obtained by the use of inductance and capacity bridges, A., ii, 7.

measurement of the electrical conductivity of solutions at different frequencies. VII. Investigations on the true and apparent resistances, voltage, apparent capacity, size and character of electrodes, ratio of inductance changes to resistance changes, and the relation of induction and capacity to frequency, A., ii, 8.

equilibrium between mucic acid and its lactones, A., ii, 133.

Tcherniac, *Joseph*, phthalonic acid and its derivatives, A., i, 33.

Teichmann, *Ernst*, the sensitiveness of strains of nagana towards arsenic and antimony, A., i, 527.

Teller, *George L.* See *J. A.* **Wesener.**

Terrisse, *H.*, preparation of phenol [from cresols], A., i, 689.

Terwen, *Johan Willem*, the allotropy of phosphorus, A., ii, 173.

Tesch, *Bruno*. See *Arthur* **Stähler.**

Thevenon and **Rolland**, the detection of blood in urine, fæcal matters, and pathological fluids, A., ii, 432.

Thévenon, *L.* See *A. Ch.* **Hollande.**

Thiel, *Alfred*, time reaction of the neutralisation of carbonic acid and the true dissociation constant of carbonic acid, A., ii, 134.

Thoburn, *T. W.* See *R. W.* **Scott.**

Thörner, *Wilhelm*, nature of the sulphur of peat soils, A., i, 76.

Thole, *Ferdinand Bernard*. See *Ernest Lawson* **Lomax.**

Thomas, *Arthur W.*, a noteworthy effect of bromides on the action of malt amylase, A., i, 598.

Thomas, *John*, separation of secondary arylamines from primary amines, T., 562; A., i, 451.

Thomas, *John Smeath*, and *Alexander* **Rule**, the polysulphides of the alkali metals. III. The solidifying points of the systems, sodium monosulphide-sulphur, and potassium monosulphide-sulphur, T., 1063.

Thomas, *Ruth M.* See *Forris Jewitt* **Moore.**

Thomlinson, *John Clark*, use of uranium in analysis, A., ii, 41.

Thompson, *F. C.*, the properties of solid solutions of metals and of intermetallic compounds, A., ii, 481.

Thompson, *Maurice de Kay*, and *N. J.* **Thompson**, electrolytic oxidation of sulphurous acid, A., ii, 137.

Thompson, *N. J.* See *Maurice de Kay* **Thompson.**

Thompson, *William Henry*, effects of intravenous injection of arginine on the creatine content of rabbits' muscle, A., i, 369.

metabolism of arginine. III. Arginine and creatine formation, A., i, 673.

Thoms, *Hermann*, preparation of thiocarbamide compounds of arsanilic acid, its homologues and derivatives, A., i, 359.

preparation of durable fruit extracts, which contain the fragrant substances and enzymes of the fruit juices in an undecomposed form, A., i, 721.

device for accelerating dialysis, A., ii, 561.

new shaking apparatus and their application, A., ii, 567.

Thoms, *Hermann,* and *P.* **Runze,** salts and esters of *d*-camphoric acid, A., i, 699.
Thoms, *Hermann,* and *Th.* **Sabalitschka,** scission of acid salts into normal salts and free acids in aqueous solutions, A., i, 700.
Thoms, *Hermann,* and *G. K. W.* **Zehrfeld,** demonstration of the scission of salts of organic acids by means of conductivity determinations, A., i, 699.
Thomsen, *Th. Sv.,* the estimation of nicotine in tobacco extract, A., ii, 431.
Thomson, *W.* See *J. F.* **McClendon.**
Thornton, *L. H. D.* See *Carl Hamilton* **Browning.**
Thornton, *William Mandell,* the relation of oxygen to the heat of combustion of organic compounds, A., ii, 164.
  limits of inflammability of gaseous mixtures, A., ii, 172.
  the nature of chemical affinity in the combustion of organic compounds, A., ii, 357.
  the curves of the periodic law, A., ii, 367.
Thugutt, *Stanislaus Józef,* microchemical examination of ittnerite and scolopsite, A., ii, 493.
  microchemical examination of zeagonite, A., ii, 494.
  a new microchemical reaction for calcite, A., ii, 508.
Thugutt, *Stanislaus Józef,* and *W.* **Koziorovski,** microchemical reactions of dolomite from Kielce, Poland, A., ii, 488.
Tillmans, *Josef,* and *O.* **Heublein,** estimation of carbon dioxide in water, A., ii, 332.
Timofeev, *G. E.,* and *V. A.* **Kravcov,** reaction between amylene and trichloroacetic acid in different solvents. II., A., ii, 134.
Timoféev, *K. J.,* petrography of the Central Caucasus, A., ii, 495.
  olivine from the Brahin meteorite, A., ii, 498.
Tingle, *Alfred,* and *Allan A.* **Ferguson,** a new method for the estimation of nicotine in tobacco, A., ii, 55.
Tinker, *Frank,* osmotic pressure: its relation to the membrane, the solvent, and the solute, A., ii, 294.
  the selective properties of the copper ferrocyanide membrane, A., ii, 363.
Tinker, *Frank.* See also *Adrian John* **Brown.**
Tixier, *Léon,* identification of picric acid in a case of feigned icterus; simple method of identifying poison in blood, A., ii, 584.
Toabe, *Kebe.* See *Arthur Amos* **Noyes.**
Tollens, *Bernhard,* the carbohydrates of lichens, A., i, 618.
Tomi, *W.* See *Hans* **Rupe.**
Tomlins, *Henry Philip.* See *Gilbert Thomas* **Morgan.**
Torossian, *Gregory,* iodometric estimation of chlorine in chlorides, A., ii, 500.
Tottingham, *W. E.* See *B. E.* **Read.**
Trapani, *Eligio,* product of deflagration of cellulose nitrate, A., i, 380.
Trautz, *Max,* the law of reaction velocity and of equilibrium in gases; the additivity of $C_v-\frac{3}{2}R$; new determinations of the integration constants and of the molecular diameter, A., ii, 23.
  the dissociation of phosphorus, and the detonating gas cell in the light of the new theory of gas reactions and a new interpretation of the appropriate additivity of $C^v-\frac{3}{2}R$ for gases, A., ii, 74.
  homogeneous equilibrium and additivity of internal atomic heats $(C_v-\frac{3}{2}R)$ in ideal gases, A., ii, 439.
  molecular heat of zinc dimethyl vapour; an example of the additive nature of $C_v-\frac{3}{2}R$, A., ii, 440.
Trautz, *Max,* and *Claus Friedrich* **Hinck,** the dissociation equilibrium of nitrosyl chloride, $2NO + Cl_2 \rightleftarrows 2NOCl$. II. Replacement of the chemical constants by integration constants calculated from the molecular dimensions, A., ii, 74.
Trautz, *Max,* and *Lili* **Wachenheim,** the dissociation equilibrium of nitrosyl chloride, $2NO + Cl_2 \rightleftarrows 2NOCl$, A., ii, 74.
Travers, rapid estimation of manganese and chromium in metallurgical products, A., ii, 511.
  new volumetric method for the estimation of molybdenum and vanadium in steels, A., ii, 545.
  a new separation of tin and tungsten in stanniferous wolframs, A., ii, 545.
Travers, *Morris William, N. M.* **Gupta,** and *R. C.* **Ray,** some compounds of boron, oxygen, and hydrogen, A., ii, 307.
Treadwell, *W. D.,* oxygen pressure of some oxides and the carbon-oxygen cell at high temperatures, A., ii, 117.
Treub, *J. P.,* the saponification of fats, A., ii, 528.
Tribondeau, *L.,* and *J.* **Dubreuil,** new stains for microscopic work derived from methylene-blue, A., i, 285.

Trimby, *J. C.* See *John Franklin* **Lyman.**
Tröger, *Julius,* and *G.* **Lange,** *p*-, *o*-, and *m*-toluene-α-naphthylhydrazinesulphonic acids, A., i, 418.
Tröger, *Julius,* and *J.* **Piotrowski,** acid additive compounds of azobenzene-*p*-hydrazones, A., i, 667.
  p-chlorobenzeneazo-α-naphthylhydrazinesulphonic acid, A., i, 669.
Trojan, *E.*, production of light by animals, A., i, 427.
Tromp, *F. J.*, steam distillation, A., ii, 193.
Tronov, *B. V.* See *Vladimir Vasilevitsch* **Tschelincev.**
Tropsch, *Hans.* See *Franz* **Fischer.**
Troussov, *A.*, humus formation as an essential property of plants, A., i, 189.
Truesdell, *H. W.*, effect of phosphorus on lucerne and lucerne bacteria, A., i, 242.
Truog, *E.*, and *J.* **Sykora,** soil constituents which inhibit the action of plant toxins, A., i, 622.
Truskier, *P.* See *Paul* **Pfeiffer.**
Tsakalotos, *Demetrius E.*, optical activity of pine species, A., i, 577.
Tschelincev, *Vladimir Vasilevitsch,* and *B. V.* **Maksorov,** condensation of pyrrole and 1-methylpyrrole with formaldehyde: preparation of glycols of the pyrrole series, A., i, 164.
  new method of preparing pyrrole-2:5-dicarboxylic acids, A., i, 165.
Tschelincev, *Vladimir Vasilevitsch,* and *B. V.* **Tronov,** process of the condensation of pyrrole with acetone, A., i, 91.
  structure of the condensation products of pyrrole and acetone, A., i, 93.
  condensation of pyrrole with methyl ethyl ketone, methyl hexyl ketone, and with acetone and methyl ethyl ketone together; its bearing on the formulæ for chlorophyll and hæmin, A., i, 411.
Tschelincev, *Vladimir Vasilevitsch, B. V.* **Tronov,** and *S. G.* **Karmanov,** condensation of pyrrole with *cyclo*hexanone, other cyclic ketones, and acetone and *cyclo*hexanone together; capacity of different ketones for condensation with pyrrole, A., i, 412.
Tschermak, *Gustav,* simultaneous separation of two forms of silicic acid from the same silicate, A., ii, 30.
Tschernik, *Georgei Prokofevitsch,* mineralogy of the Island of Borneo, A., ii, 484.
Tschischovsky, *N.*, and *A.* **Herdt,** iron and boron, A., ii, 372.
Tschugaev, *Leo Alexandrovitsch,* and *Stanislav Stanislavovitsch* **Kiltinovic,** ammoniacal derivatives of platinous nitrile, A., ii, 96.
Tsudji, *M.*, asymmetric splitting of racemic tyrosine by *Bacillus proteus vulgaris* and *Bacillus subtilis* (biological method of preparing *d*-tyrosine), A., i, 679.
Tunmann, *Otto,* secretions in the rhizome of rheum; a contribution to the microchemistry of the hydroxymethylanthraquinone-bearing plants, A., i, 531.
  microchemistry of plants. XIV. Identification of crocetin, A., ii, 58.
  microchemistry of æsculin and its detection in *Æsculus hippocastanum,* A., ii, 59.
  identification of opium with the aid of meconine and meconic acid, A., ii, 226.
  microchemical precipitation of alkaloids with zinc chloride-iodine solution, A., ii, 345.
  microchemical reactions of sparteine, A., ii, 518.
  identification of the poisons extractable from acid aqueous solution by means of ether according to the Stas-Otto process (veronal, acetanilide, salicylic acid, phenacetin), A., ii, 551.
Turkus, (*Mlle.*) *Bronislava,* estimation of potassium and sodium in the form of sulphates by platinum chloride, A., ii, 385.
Turkus, (*Mlle.*) *Bronislava.* See also *Siegmund* **Reich.**
Turner, *Eustace Ebenezer,* studies in ring formation. II. The action of aromatic amines on acetylacetone and benzoylacetone, T., 1; A., i, 130.
  the "cyclic theory" of the constitution of complex inorganic compounds: a criticism, A., ii, 28.
Tutton, *Alfred Edwin Howard, X*-ray analysis and topic axes of the alkali sulphates and their bearing on the theory of valency volumes, A., ii, 244.
  monoclinic double selenates of the nickel group, A., ii, 415.
Twiss, *Douglas Frank,* and *W.* **McCowan,** a modified Soxhlet extractor, A., ii, 418.
Twitchell, *Ernest,* composition of menhaden oil fatty acids, A., ii, 428.
Twomey, *Thomas J.* See *Gustav* **Egloff.**

U.

Ubbelohde, *Leo*, and *R.* **Anwandter**, the Bunsen flame under diminished pressure, A., ii, 569.

Uhl, *Alfred*. See *Franz Wilhelm* **Dafert.**

Uhler, *Horace S.*, and *Philip Embury* **Browning**, electrolysis and purification of gallium, A., ii, 34.

Uibrig, *Cl.* See *Kurt* **Hess.**

Ulbrich, *E.* See *Adolf* **Grün.**

Ullmann, *Fritz*, a new method for preparing cyclic ketones, A., i, 342.

Ullmann, *Fritz*, and *Otto von* **Glenck**, the thioxanthone- and benzophenone-sulphone series, A., i, 159.

Underhill, *Frank Pell*. See *Louise* **McDanell.**

Union Carbide Co., preparation of acetaldehyde, A., i, 318.

Upson, *Fred. W.*, *H. M.* **Plum**, and *J. E.* **Schott**, the Duclaux method for the estimation of the volatile fatty acids, A., ii, 277.

Upton, *Adolph William Henry*. See *Gilbert Thomas* **Morgan.**

Urbain, *Édouard*, a method of determining molecular weights, A., ii, 407.

Ursprung, *A.*, formation of starch [in plants exposed] in the spectrum, A., i, 504.

Usher, *Francis Lawry*, and *Basrur Sanjiva* **Rao**, the determination of ozone and oxides of nitrogen in the atmosphere, T., 799 ; A., ii, 502.

V.

Valentin, *Franz*, production of cholesterol esters in fatty degeneration, A., i, 715.

Valeton, *A. M.* See *Ernst* **Cohen.**

Valeur, *Amand*, an anomaly in the solubility of sparteine, A., i, 411.

Vanino, *Ludwig*, the use of citarin in scientific chemistry, A., ii, 299.
  history and preparation of cobalt hygrometers, A., ii, 320.

Vanino, *Ludwig*, and *F.* **Bertele**, estimation of sugar in urine, A., ii, 342.

Vanino, *Ludwig*, and *F.* **Mussgnug**, organic double compounds of the bismuth haloids, A., i, 196.
  preparation of a basic bismuth chlorate, A., ii, 264.

Veen, *A. L. W. E. van der*, the crystalline form of diphenyliodonium chloride, $C_{12}H_{10}ICl$, A., i, 548.

Vegard, *L.*, results of crystal analysis. IV. The structure of ammonium iodide, tetramethylammonium iodide, and xenotime, A., ii, 296.

Vegard, *L.*, and *H.* **Schjelderup**, the constitution of mixed crystals, A., ii, 243.

Vegezzi, *G.* See *Charles* **Dhéré.**

Venable, *Francis P.*, and *James Munsie* **Bell**, atomic weight of zirconium, A., ii, 479.

Vendl, *Al.*, stilbite and chabazite from Hungary, A., ii, 493.

Verkade, *P. E.*, complex organic manganese compounds. II., A., i, 377.

Verschaffelt, *Jules Émile*, the viscosity of liquefied gases. VI. Observations on the torsional oscillatory movement of a sphere in a viscous liquid with finite angles of deviation and application of the results obtained to the determination of viscosities. VII. The torsional oscillatory motion of a body of revolution in a viscous liquid. VIII. The similarity in the oscillatory rotation of a body of revolution in a viscous liquid, A., ii, 408.

Verschaffelt, *Jules Émile*, and *Ch.* **Nicaise**, the viscosity of liquefied gases. IX. Preliminary determination of the viscosity of liquid hydrogen, A., ii, 408.

Vesterberg, *Karl Albert*, a chemical method of determining the strength of sparingly soluble inorganic bases, A., ii, 248.
  the hydrolysis of cobalt and nickel acetate, A., ii, 263.

Viehoever, *Arno*. See *Lewis H.* **Chernoff.**

Vigreux, *Henri*, a removable, universal condenser, A., ii, 198.

Villedieu and **Hébert**, estimation of ethyl alcohol in dilute solutions (0·1 to 1%) ; application of the method to urine, A., ii, 155.

Viola, *Carlo*, mixed crystals, $(Mg,Zn)SO_4,7H_2O$, A., ii, 79.
  Gibbs's phase rule, A., ii, 80.
  mixed crystals, A., ii, 297.

Vivario, *R.*, and *Marius* **Wagenaar**, urotropine [hexamethylenetetramine] as a micro-chemical reagent, A., ii, 179.

Voano, *V.*, equilibrium of the binary mixture, phenol–aniline, near the distectic point, A., ii, 81.

Voegtlin, *Carl*, and *Carl P.* **Sherwin**, adenine and guanine in cows' milk, A., i, 366.

Vogel, *Rudolf*, cerium–iron alloys, A., ii, 259.

Volchonski, *E.*, principle of the change of an equilibrated system under the influence of an external agent. II., A., ii, 133.

Volmer, *Max*, photoelectric ionisation of solutions, A., ii, 353.

Vondráček, *Rudolf*, numerical relationships between atomic weights, A., ii, 460.

Voroschov, *Nicolai N.*, the bisulphite compounds of azo-colouring matters, A., i, 300.

Vosburgh, *Isabella*, the molecular rearrangement of triphenylmethylhalogenamines, A., i, 20.

Vosburgh, *W. C.* See *John Maurice* **Nelson.**

Votoček, *Emil*, derivatives of rhodeose (degradation of rhodeose), A., i, 250.
estimation of phloroglucinol and resorcinol by means of furfuraldehyde, A., ii, 156.

Votoček, *Emil*, and *B.* **Röhlich**, fucose or fucosan in *Fucus virsoides*, A., i, 438.

Vries, *J. J. Ott de.* See *Fritz Willem Jacob* **Boekhout.**

Vuaflart, *L.*, detection of arsenic by means of mercuric chloride paper, A., ii, 331.

Vürtheim, *A.*, recovery of perchlorate residues obtained in potassium estimations, A., ii, 568.

Vulquin, *E.*, and *M.* **Entat**, detection and estimation of small quantities of free sulphuric acid in the presence of sulphates, A., ii, 268.

W.

Wachenheim, *Lili.* See *Max* **Trautz.**

Wadsworth, *Charles, 3rd.* See *Theodore William* **Richards.**

Wagenaar, *Marius.* See *R.* **Vivario.**

Wagner, *A.* See *Alexander* **Gutbier.**

Wagner, *Paul.* See *Fritz* **Ephraim.**

Wahl, *André*, the solvents of coal, A., ii, 324.

Wakeman, *Alfred John.* See *Thomas Burr* **Osborne.**

Waksman, *Selman A.*, influence of available carbohydrates on ammonia accumulation by micro-organisms, A., i, 613.

Waldstein, *P. J.* See *H. A.* **Scholz.**

Walker, *Herbert S.*, simplified inversion process for the estimation of sucrose by double polarisation, A., ii, 395.

Walker, *Jennie A.* See *Henry Clapp* **Sherman.**

Walker, *R. M.*, colloidal nature of the Wassermann reaction, A., i, 527.

Walker, *Thomas Leonard*, mineral occurrences in the Worthington Mine, Sudbury, Ontario, A., ii, 486.

Wallerant, *Frédéric* [*Félix Auguste*], polymorphism of ammonium nitrate, A., ii, 470.

Walsh, *J. W. T.*, the theory of decay in radioactive luminous compounds, A., ii, 559.

Walters, *A. L.*, *C. R.* **Eckler**, and *E. W.* **Koch**, pharmacological studies of the ipecacuanha alkaloids and some synthetic derivatives of cephaeline. II. Emetic effect and irritant action, A., i, 717.

Walters, *A. L.*, and *E. W.* **Koch**, pharmacological studies of the ipecacuanha alkaloids and some synthetic derivatives of cephaeline. I. Toxicity, A., i, 612.

Walters, *E. H.*, and *Louis Elsberg* **Wise**, *α*-crotonic acid, a constituent of the soil, A., i, 376.

Walters, *E. H.* See also *Louis J.* **Gillespie**, and *Louis Elsberg* **Wise.**

Wandenbulke, *F.* See *F.* **Dienert.**

Wang, *Chi Che.* See *Katharine* **Blunt.**

Wanjukow, *W.* See *H. O.* **Hofman.**

Ward, *A. L.* See *R. S.* **Boehner.**

Ward, *T. J.*, treatment of corks used in Soxhlet and other extraction apparatus, A., ii, 538.

Warren, *Charles H.*, and *John A.* **Allan**, [with analysis by *M. F.* **Conner**], titaniferous augite from Ice River, British Columbia, A., ii, 149.

Waser, *Ernst*, detection and estimation of formic acid in meat extract, A., ii, 343.

Washburn, *Edward Wight*, measurement of electrolytic conductivity. I. Theory of the design of conductivity cells, A., ii, 10.

Washburn, *Edward Wight*, and *Karr* **Parker**, the measurement of electrolytic conductivity. II. The telephone receiver as an indicating instrument for use with the alternating current bridge, A., ii, 235.

Wastenson, *Hugo*, estimation of mercury in galenical preparations, A., ii, 509.

Watanabe, *C. K.* See *Thomas* **Addis.**

Watanabe, *Hikohei.* See *Mitsuru* **Kuhara.**

Waterman, *A. T.*, positive ionisation of certain hot salts, together with some observations on the electrical properties of molybdenite at high temperatures, A., ii, 162.

Waterman, *Hein Israel*, the metabolism of *Aspergillus niger*, A., i, 73.
influence of aminoacetic acid and *α*-aminopropionic acid on the action of alkali on dextrose, A., i, 195.

Waterman, *Hein Israel*, amygdalin as nutriment for *Aspergillus niger*, A., i, 502, 530.
  spontaneous infection of a saturated potassium chlorate solution, A., i, 502.
  influence of different compounds on the destruction of monosaccharides by sodium hydroxide and on the inversion of sucrose by hydrochloric acid; constitutional formula of α-amino-acids and of betaine, A., i, 631.

Watson, *Edwin Roy*. See *Praphulla Chandra* **Ghosh**.

Watson, *J. W.* See *Thomas Leonard* **Watson**.

Watson, *Thomas*. See *Henry Chalmers* **Biddle**.

Watson, *Thomas Leonard*, and *J. W.* **Watson**, mineralogy of Graves Mountain, Georgia, A., ii, 493.

Weber, *Friedl*, viscosimetry of living protoplasm, A., i, 504.

Wedekind & Co., *E.*, preparation of benzoyl derivatives of β-hydroxy- or $\alpha\beta$-di- and poly-hydroxyanthraquinones, A., i, 464.

Weeks, *L. F.* See *Roger* **Adams**.

Weeks, (*Miss*) *Mary Elvira*. See *Joseph Howard* **Mathews**.

Weerman, *Rudolf Adriaan*, action of sodium hypochlorite on amides of α-hydroxy-acids and of polyhydroxy-acids having a hydroxyl group in the α-position; a new method for the degradation of sugars, A., i, 546.
  the hydrazides of acids produced by the oxidation of sugars, A., i, 548.
  the action of sodium hypochlorite on amides of unsaturated acids, A., i, 560.

Weevers, *Theodorus*, the physiological significance of potassium in plants, A., i, 372.

Wegelin, *Gustav*, an arrangement for the automatic washing of precipitates filtered with difficulty, A., ii, 462.

Wehmer, *Carl*, action of illuminating gas on plants. I. Action of the gas on the germination of spores and seeds, A., i, 507.
  action of coal gas on plants. II. Action on green plants, A., i, 531.
  action of coal gas on plants. III. Action of coal gas, whilst passing through soil or water, on roots and leafy branches, A., i, 618.

Wehrung. See *Émile* **Saillard**.

Weil, *Friedrich Josef*. See *Richard* **Willstätter**.

Weilenmann, *Max*. See *Friedrich* **Kehrmann**.

Weimarn, *Petr Petrovitsch von*, structure of true solutions and nature of the transformations occurring in them, A., ii, 126.
  general method for obtaining metals in a metalloidal condition, A., ii, 313.

Weinland, *Rudolf Friedrich*, *A.* **Alber**, and *J.* **Schweiger**, double salts of bismuth trichloride and chlorides of bivalent metals, A., ii, 374.

Weinland, *Rudolf Friedrich*, and *Edmund* **Bässler**, iron-acetylacetone-pyridine compounds, A., i, 6.

Weinland, *Rudolf Friedrich*, and *Kurt* **Zimmermann**, iron compounds of salicylic acid, A., i, 649.

Weise, *G. L.* See *Alexander* **Gutbier**.

Weiser, *Harry B.*, the physical character of precipitated lead molybdate and its importance in the estimation of molybdenum and lead, A., ii, 105.
  the luminescence of the iodide of Millon's base, A., ii, 174.
  effect of adsorption on the physical character of precipitated barium sulphate, A., ii, 311.

Weiss, *John Morris*, and *C. R.* **Downs**, estimation of phenol in crude carbolic acid and tar oils, A., ii, 427.

Weiss, *Moriz*, the estimation and nature of urochromogen, A., ii, 431.

Weiss, *Morris L.* See *Isidor* **Greenwald**.

Weiss, *Rich.*, quantitative estimation of ammonia and sulphur compounds in urine, A., ii, 217.

Weitzel, *A.*, volumetric estimation of chlorine in foods, etc., without formation of ash, by the wet method, A., ii, 501.

Weller, *Johannes*. See *William* **Küster**.

Wellisch, *Edward Montague*, the motion of ions and electrons through gases, A., ii, 352.

Wells, *Harry Gideon*, antigenic properties of β-nucleoproteins, A., i, 98.

Wells, *Lansing S.* See *W. G.* **Bateman**.

Wells, *Roger Clark*, and *Esper Signius* **Larsen**, lorettoite, a new mineral, A., ii, 96.

Wempe, *Georg*, an air-tight gas collecting tube without stopcock, A., ii, 529.

Wenzel, *Franz*. See *Josef* **Herzig**.

Werner, *Emil Alphonse*, methylation by means of formaldehyde. I. Mechanism of the interaction of formaldehyde and ammonium chloride; the preparation of methylamine and dimethylamine, T., 844; A., i, 632.

Werner, *Emil Alphonse*, the constitution of carbamides. IV. The mechanism of the interaction of carbamide [urea] and nitrous acid, T., 863; A., i, 639.

the constitution of carbamides. III. The reaction of urea and of thiourea with acetic anhydride; potassium thiourea, A., i, 11.

preparation of cyanamide from calcium cyanamide, A., i, 82.

Werner, *Louis F.* See *Lauder William* **Jones.**

Wesche, *Hans.* See *Richard* **Meyer.**

Wesener, *J. A.*, and *George L.* **Teller,** composition of commercial glucose and its digestibility, A., i, 7.

Wesson, *L. G.*, carbon dioxide absorption apparatus, A., ii, 332.

Wesson, *L. G.*, and *E. S.* **Knorr,** wet combustion in the nitrosite combustion method for the direct estimation of caoutchouc, A., ii, 341.

West, *Clarence J.* See *Phœbus A.* **Levene.**

Westerlund, *A.*, vital oxidation of succinic acid; the chemical kinetics of a physiological process, A., i, 68.

Westgren, *Arne*, determinations of the compressibility of disperse systems, A., ii, 452.

Weston, *Paul G.*, colorimetric methods for estimating cholesterol in serum, A., ii, 156.

Wheeler, *Edward G.*, the stem correction of thermometers, A., ii, 65.

Wheeler, *Richard Vernon*, the influence of pressure on the ignition of a mixture of methane and air by the impulsive electrical discharge, T., 411; A., ii, 300.

Wheeler, *Richard Vernon*, and *Allan* **Greenwell,** "stepped" ignition, T., 130; A., ii, 171.

Wheeler, *Richard Vernon*, and *Arnold* **Whitaker,** propagation of flame in mixtures of acetone and air, T., 267; A., ii, 249.

Wheeler, *Richard Vernon.* See also *Walter* **Mason.**

Wheelwright, *Edwin Whitfield*, obituary notice of, T., 377.

Wherry, *Edgar Theodore*, neodymium as the cause of the red-violet colour in certain minerals, A., ii, 209.

Wherry, *Edgar Theodore*, and *Glenn V.* **Brown,** an American occurrence of miloschite, A., ii, 148.

Wherry, *Edgar Theodore.* See also *Esper Signius* **Larsen.**

Whitaker, *Arnold.* See *Richard Vernon* **Wheeler.**

White, *E. C.*, and *Solomon Farley* **Acree,** quinone-phenolate theory of indicators; electrical conductivity of solutions of phenolsulphonephthalein and of its bromo- and nitro-derivatives, A., i, 340.

Whitfield, *J. E.* See *George Perkins* **Merrill.**

Wibaut, *Johan Pieter*, formation of amine from ammonia and benzene at high temperatures, and in the presence of contact catalysts, A., i, 386.

Widman, *Oskar*, action of hydroxylamine and hydrazine on benzoylphenylethylene oxide, A., i, 221.

Widmark, *Erik Matteo Prochet*, modification of the Nicloux method for estimating ethyl alcohol, A., ii, 547.

some measurements of the alcohol content of the urine in intoxicated persons, A., ii, 547.

Wiechowski, *Siegfried*, lecture experiment: preparation of sodium, A., ii, 568.

Wiechowski, *Wilhelm*, the "mechanical denaturation" of proteins and the method of drying organs for biological investigation, A., i, 520.

Wiedmann, *Gebhard*, the influence of different gases on the photo-electricity of potassium, A., ii, 6.

Wiegner, *George*, the refractive power and the specific refraction of dispersoids, A., ii, 185.

Wieland, *Heinrich*, and *Hermann* **Sorge,** bile acids. III. Structural relations between cholic and deoxycholic acids, A., i, 685.

Wiener, *Adele*, the microchemical detection of iron, especially that contained in the "masked" form in plants, A., ii, 44.

Wiessmann, *H.* See *Alexander* **Gutbier.**

Wild, *Samuel.* See *Hans* **Rupe.**

Wilder, *Russell M.*, intravenous injections of β-hydroxybutyric and acetoacetic acids, A., i, 611.

Wilenko, *Gerson G.*, glycolysis, A., i, 680.

Wiley, *J. A.* See *George Leslie* **Kelley.**

Wilkie, *John Matthew*, estimation of unsaponifiable matter in oils, fats, and waxes, A., ii, 429.

Wilkie, *John Matthew*, and *H. S.* **Anderson,** soluble filters and filtering media, A., ii, 224.

Wilkins, *Lawson.* See *Herbert A.* **Lubs.**

Wilkoszewski, *Bogumil de*, an agronomic study of several fertilising or anticryptogamic compounds used in agriculture, A., i, 723.

Willaman, *J. J.*, estimation of hydrocyanic acid and the probable form in which it occurs in *Sorghum vulgare*, A., i, 245.

effect of anæsthetics and of frosting on the cyanogenetic compounds of *Sorghum vulgare*, A., i, 246.

modification of the Pratt method for the estimation of citric acid, A., ii, 51.

Willcox, *Marguerite*, and *Roger Frederick* **Brunel**, the molecular weight of some alcoholates of chloral and butylchloral in benzene solution, A., i, 5.

Williams, *A. M.*, the adsorption of sulphur dioxide by charcoal at −10°, A., ii, 362.

Williams, *C. M.*, X-ray analysis of the crystal structure of rutile and cassiterite, A., ii, 450.

Williams, *Gwilym*, hydrolysis of the soluble protein of swede turnips, A., i, 375.

Williams, *Howell*, electrolytic valuation of iron sulphide, A., ii, 425.

Williams, *J. L.* See *C. Ferdinand* **Nelson.**

Williams, (*Miss*) *Margaret Mary*. See (*Miss*) *Annie Mary Bleakly* **Orr**, and *John* **Read.**

Williams, *P.* See *Richard* **Seligman.**

Williams, *Robert R.*, chemical nature of the "vitamines." III. Structure of the curative modifications of the hydroxypyridines, A., i, 353.

Williams, *Robert Stenhouse*. See *Elfrida Constance Victoria* **Cornish.**

Williamson, *E. D.* See *John* **Johnston.**

Willis, *L. G.* See *W. H.* **MacIntire.**

Willstätter, *Richard*, and *Elmer Keiser* **Bolton**, anthocyanins. XI. The anthocyanin of red-flowering varieties of *Salvia*, A., i, 42.

anthocyanins. XII. Anthocyanin of the winter aster (*Chrysanthemum*), A., i, 43.

Willstätter, *Richard*, and *Ch. L.* **Burdick**, anthocyanins. XIII. Two anthocyanins of the summer aster, A., i, 44.

anthocyanins. XVII. The colouring matter of the petunia, A., i, 49.

Willstätter, *Richard*, and *Friedrich Josef* **Weil**, anthocyanins. XV. Anthocyanin of the pansy, A., i, 46.

anthocyanins. XVIII. Colouring matter of the poppy. I., A., i, 49.

Willstätter, *Richard*, and *Ernst H.* **Zollinger**, anthocyanins. XIV. Colouring matter of the cherry and of the sloe, A., i, 45.

anthocyanins. XVI. Colouring matter of the grape and of the bilberry, A., i, 47.

Wilson, *D. Wright*, and *Edward F.* **Adolph**, partition of non-protein nitrogen in the blood of fresh-water fish, A., i, 360.

Wilson, *D. Wright*, and *E. D.* **Plass**, creatine and creatinine in whole blood and plasma, A., i, 360.

Wilson, *John Arthur*. See *Henry Richardson* **Procter.**

Wilson, *J. B.* See *Frank C.* **Cook.**

Windaus, *Adolf*, cholesterol. XXV., A., i, 265.

diverse physiological behaviour of certain stereoisomeric alcohols of the cholesterol series, A., i, 610.

Windaus, *Adolf*, and *Daisy* **Bernthsen-Buchner**, synthesis of 4-hydroxy-1-β-aminoethylnaphthalene [4-β-aminoethyl-α-naphthol], A., i, 690.

Winkler, *Ludwig Wilhelm*, the correction values in the estimation of free carbon dioxide in water, A., ii, 423.

water analysis. IV., A., ii, 501.

analysis of ferrum hydrogenio reductum, A., ii, 511.

Winterfeld, *Georg*. See *Otto* **Ruff.**

Winterstein, *Hans*, narcosis, A., i, 68.

Wischo, *Fritz*, identification of chlorates in the presence of hypochlorites, A., ii, 539.

Wise, *Louis Elsberg*, elimination of malates after subcutaneous injection of sodium malate, A., i, 105.

a simplified micro-combustion method for the estimation of carbon and hydrogen, A., ii, 541.

Wise, *Louis Elsberg*, and *E. H.* **Walters**, isolation of cyanuric acid from soil, A., i, 622.

Wise, *Louis Elsberg*. See also *William* **Salant**, and *E. H.* **Walters.**

Wislicenus, *Wilhelm*, [with *Kurt* **Börner**, *Paul* **Kurtz**, and *Ernst A.* **Bilhuber**], isomerism of formylphenylacetic esters. IV. Methyl formylphenylacetate, A., i, 268.

Wislicenus, *Wilhelm*, and *Karl* **Eble**, desmotropic forms in the series of oxalacetic ester derivatives, especially of ethyl diphenylmethyloxalacetate [α-oxalo-ββ-diphenylpropionate], A., i, 271.

Wislicenus, *Wilhelm*, and *Heinrich* **Elvert**, ester condensations with naphthylacetic esters, A., i, 202.

Wislicenus, *Wilhelm*, and *Hugo* **Pfannenstiel**, indandione and bindone. I. Aniline derivatives of indandione, A., i, 273.

Wislicenus, *Wilhelm*, and *Hermann* **Schneck**, indandione and bindone. II. Action of aromatic amines on bindone, A., i, 274.

Wislicenus, *Wilhelm*, and *Karl* **Schöllkopf**, condensation of ethyl oxalate with ethyl ethoxycrotonate, ethoxypropene, and acetonediethylacetal, A., i, 700.

Wisselingh, *C. van*, detection and presence of carotinoids in plants, A., ii, 554.

Withrow, *James R.* See *Orland R.* **Sweeney.**

Witt, *J. C.*, analysis of Babbit metal, A., ii, 335.
  testing of galvanised iron, A., ii, 337.

Witzemann, *Edgar John*, the preparation of glycollic acid, A., i, 316.
  variation in the physical properties of precipitated and colloidal manganese dioxide from the point of view of physical chemical equilibrium, A., ii, 262.

Wodehouse, *R. P.*, direct estimations of permeability, A., i, 371.

Wöber, *A.*, volumetric estimation of polysulphide, monosulphide, and thiosulphate sulphur in lime–sulphur liquids, A., ii, 503.

Wöhler, *Lothar*, and *F.* **Martin**, new fulminates and azides, A., i, 383.
  the sensitiveness of azides, A., ii, 466.

Wöhler, *Lothar*, and *W.* **Prager**, determination of the heterogeneous equilibrium of water vapour, particularly in the case of iron and tungsten, A., ii, 455.

Woernle, *M.* See *Alexander* **Gutbier.**

Wohack, *Franz.* See *Maximilian* **Ripper.**

Wohl, *Alfred*, and *Fr.* **Momber**, the sterical relationships between glyceraldehyde and tartaric acid, A., i, 319.

Woker, *Gertrud*, formaldehyde as a prototype of diastase; theory of the action of diastase, A., i, 61.
  theory of the oxidation of benzidine in its significance for peroxydase investigations, A., i, 62, 485.
  the reaction between starch and formaldehyde, and the diastatic properties of formaldehyde, A., i, 447.
  [aldehyde hypothesis of the peroxydases], A., i, 485.

Woker, *Gertrud*, and *H.* **Maggi**, formaldehyde as a hydrogenase model, and some observations on formaldehyde condensations, A., i, 686.

Woker, *Gertrud.* See also *H.* **Maggi.**

Wolf, *Charles George Lewis*, and *Walter Craven* **Ball**, estimation of sugar in blood, A., ii, 106.

Wolf, *Kuno*, modification of Fehling's method for the estimation of sugar, A., ii, 514.

Wolff, *G.* See *Franz* **Lehmann.**

Wolff, *Hans*, detection of small quantities of glycerol, A., ii, 512.

Wolff, *Jules*, biochemical reactions for distinguishing between the three isomeric dihydroxybenzenes: catechol, quinol, and resorcinol, A., ii, 182.

Wolff, *Jules*, and *B.* **Geslin**, the diastatic degradation of inulin in chicory root, A., i, 720.

Wolffenstein, *R.* See *Adolf* **Loewy.**

Wolf-Joachimowitz, *Alice*, prevention of loss of ammonia in the estimation of nitrogen by Kjeldahl's method, A., ii, 217.

Wolkoff, *M. I.*, soil colloids. II. Influence of colloids on electrical conductivity of salts, A., i, 621.
  adsorption of ammonium sulphate by soils and quartz sand, A., i, 622.

Woodhouse, (*Mrs*) *Hilda.* See *William Smith* **Denham.**

Woodyatt, *Rollin Turner.* See *W. D.* **Sansum.**

Woollett, *G. H.*, the silver salt of triiodophenol and its catalytic decompositions, A., i, 25.

Worley, *Frederick Palliser*, and *Vere Rochelle* **Browne**, the hydrolysis of sodium cyanide, T., 1057.

Worrall, *David E.*, the action of the tolylthiocarbimides on sodiophenylacetylene, A., i, 335.

Wratschko, *F.*, a new reaction for the water-soluble, active glucoside from digitalis leaves, A., ii, 182.

Wrede, *Fritz.* See *Wilhelm* **Schneider.**

Wren, *Henry*, and *Charles James* **Still**, the phenylsuccinic acid series. IV. *l*-Menthyl esters of the diphenylsuccinic acids, T., 513; A., i, 456.
  the phenylsuccinic acid series. V. The inter-conversion of the esters of *r*- and *meso*-diphenylsuccinic acids, T., 1019.

Wright, *Frederic Eugene*, crystallographic and optic properties of mannoketoheptose and of the osazones of mannoketoheptose and mannoaldoheptose, A., i, 119.
  crystallisation of menthol, A., i, 576.

Wright, *J. R.*, and *George W.* **Heise**, radioactivity of Philippine waters, A., ii, 560.

Wright, *Robert*, "spark-lengths" in various gases and vapours, T., 643; A., ii, 403.
molecular weight determinations in bromine by the air-current method, A., ii, 28.

Wright, *Robert*. See also (*Miss*) *Elizabeth* **MacDougall,** and *Alfred Walter* **Stewart.**

Wrightson, *John*, obituary notice of, T., 378.

Wroth, *B. B.*, and *Ebenezer Emmet* **Reid,** solubilities of liquids in liquids; partition of the lower alcohols between water and cotton-seed oil, A., ii, 17.

Wülfing, *Ernst Anton*, and *Friedrich* **Hörner,** staurolite, A., ii, 325.

Würschmidt, *J.*, enantiotropy of bismuth, A., ii, 323.

Wuertz, *Alexander J.* See *Ross Aiken* **Gortner.**

Wybert, *Ernst*. See *Emil* **Abderhalden.**

Wykes, *Frederick Henry*. See *Arthur* **Lapworth.**

Wynne, *William Palmer*, chemical investigation of rain water collected at various sites in the [Sheffield] city area, A., i, 108.

Y.

Yamauchi, *Yoshindo*. See *Masumi* **Chikashige.**

Yanovsky, *E.* See *Claude S.* **Hudson.**

Yarrow, *George*. See *Aquila* **Forster.**

Ydrac, detection of picric acid in urine by the *iso*purpurate reaction, A., ii, 51.

Yoshida, *Usaburo*. See *Toshio* **Takamine.**

Young, *Stewart Woodford*, and *Win R.* **Goddard,** the reversibility of sulphide sols and the protective action of hydrogen sulphide, A., ii, 167.

Young, *Stewart Woodford*, and *Roland* **Neal,** colloidal solutions of copper sulphide, A., ii, 167.

Z.

Zacharski, *J.* See *St.* **Opolski.**

Zaleski, *Jean*, chemistry of the colouring matter of the blood, A., i, 485.

Zalkind, *J. S.*, and *N. I.* **Egorkin,** preparation of hide powder, A., ii, 160.

Zalkind, *J. S.*, and (*Mlle.*) *V.* **Markarjan,** union of hydrogen with acetylenic derivatives; hydrogenation of dimethyldiethylbutinenediol [$\gamma\zeta$-dimethyl-Δ-octinene-$\gamma\zeta$-diol], A., i, 113.

Zanden, *J. M. van der*. See *Pieter van* **Romburgh.**

Zanetti, *Joaquin Enrique*, and *Gustav* **Egloff,** the thermal decomposition of benzene, A., i, 327.
aromatic hydrocarbons from the thermal decomposition of natural gas condensate, A., i, 450.

Zarzecki, *Thadäus von*. See *Kurt* **Hoesch.**

Zawidzki, *Jan* [*Wiktor Tomasz*] *von*, chemical dynamics of autocatalytic processes. I. Kinetic theory of autocatalysis and its experimental examination, A., ii, 82.

Zawidzki, *Jan von*, and *Tadeusz* **Mieczyński,** rate of hydrolysis of potassium cyanide in aqueous solution, A., ii, 81.

Zawidzki, *Jan von*, and *Wilhelm* **Staronka,** chemical dynamics of autocatalytic processes. II. Rate of isomerisation of triethyl phosphite, A., ii, 83.

Zawidzki, *Jan von*, and *Janusz* **Zaykowski,** chemical dynamics of autocatalytic processes. IV. Rate of hydrolysis of potassium methyl sulphate, A., ii, 84.

Zay, *C.*, estimation of sulphur in pyrites, A., ii, 328.

Zaykowski, *Janusz*. See *Jan von* **Zawidzki.**

Zehenter, *Josef*, *p*-hydroxytolylsulphone, A., i, 134.

Zehrfeld, *G. K. W.* See *Hermann* **Thoms.**

Zeitler, *H.*, proof of the formation of water by the union of an acid and a base to yield a salt, A., ii, 463.

Zies, *Emanuel George*, *Eugene Thomas* **Allen,** and *Herbert Eugene* **Merwin,** some reactions involved in secondary copper sulphide enrichment, A., ii, 91.

Zilva, *Sylvester Solomon*. See *Arthur* **Harden.**

Zimmerli, *William F.* See *Theodor* **Curtius.**

Zimmermann, *Kurt*. See *Rudolf Friedrich* **Weinland.**

Zincke, *Theodor*, and *K.* **Arnold,** 3-thiol-*p*-cresol, A., i, 263.

Zincke, *Theodor*, and *Grete* **Schürmann,** naphthasultam. II. Naphthasultamquinone and its derivatives, and ketochlorides of tetrahydronaphthasultam, A., i, 38.

Zinn, *John B.*, estimation of carbon dioxide in carbonates by diminished pressure, A., ii, 270.

Zirkel, *H.* See *Alfred* **Heiduschka.**

Zironi, *Amilcare*, biochemical activity of agglutinated bacteria, A., i, 680.

Zollinger, *Ernst H.* See *Richard* **Willstätter**.

Zsigmondy, *Richard*, coagulation, A., ii, 366.

Zsigmondy, *Richard*, [with *C.* **Hiege**, and *Josef* **Reitstötter**], the nucleus method for the preparation of colloidal metallic solutions of definite properties, A., ii, 364.

Zucker and **Ruge**, technique of the diazo- and urochromogen-reactions, A., ii, 112.

Zuntz, *Nathan*, the "new" method of Gad-Andresen for estimation of carbon monoxide in the blood, A., ii, 384.

Zvereva, (*Mlle.*) *A. V.* See *A. V.* **Dumanski**.

Zwaardemaker, *Hendrik*, specific smell intensity and the electrical phenomenon of cloud-like condensed water vapours in chemical series, A., ii, 65.

Zwaardemaker, *Hendrik*, and *T. P.* **Feenstra**, radium as a substitute, to an equiradio-active amount, for potassium in the so-called physiological fluids, A., i, 241.

Zyl, *J. P. van*, soil solution, A., i, 439.

Anonymous, sensitive reaction of the alkaloids of the *Solanaceae*, A., ii, 160.

INDEX OF SUBJECTS.

TRANSACTIONS AND ABSTRACTS.

1917.

(Marked T., and A., i and A., ii respectively.)

A.

Abietic acids, optically active (Schulz), A., i, 649.
Absorption apparatus. See Gas-absorption apparatus.
Acetals, preparation of (King and Mason), A., i, 5.
Acetaldehyde, preparation of, from acetylene (Dreyfus), A., i, 2; (Union Carbide Co.), A., i, 318.
  preparation of acetic acid from (Badische Anilin- & Soda-Fabrik), A., i, 377.
Acetaldehyde-ammonia, action of, on quinones (Ghosh), T., 608; A., i, 517.
Acetanilide, velocity of hydrolysis of (Merrill and Adams), A., ii, 457.
  detection of, microchemically (Tunmann), A., ii, 552.
  estimation of, in presence of salol (Dox and Plaisance), A., ii, 53.
Acetanilide, amino-, chloroacetyl derivatives (Jacobs and Heidelberger), A., i, 583.
  *di*bromoiodo- (Sudborough and Lakhumalani), T., 47.
Acethydrazide, amino-, acetyl derivative, and its derivatives (Curtius and Zimmerli), A., i, 201.
Acethydroxamic acid, amino-, *di*- and *tri*-chloro-, and their derivatives (Jones and Sneed), A., i, 326.
  bromo-, chloro-, and iodo-, and their derivatives (Jones and Werner), A., i, 381.
Acetic acid, preparation of, from acetaldehyde (Badische Anilin- & Soda-Fabrik), A., i, 377.
  preparation of, from acetylene (Dreyfus), A., i, 2.
  molecular condition of, in benzene (Beckmann, Liesche, and Gabel), A., ii, 564.
Acetic acid, action of, on aluminium (Seligman and Williams), A., ii, 317.
  replacement of, as a reagent in analysis (Bäck), A., ii, 520.
Acetic acid, bismuth salt (Salkowski), A., i, 316.
  cobalt and nickel salts, hydrolysis of (Vesterberg), A., ii, 263.
  copper salt, electrical conductivity of, in pyridine (Mathews and Johnson), A., ii, 289.
  basic lead salt, action of, on impure sugar solutions (Pellet), A., i, 8.
Acetic acid, benzyl and ethyl esters, compounds of thiocarbamide and (Taylor), T., 662; A., i, 514.
  *tri*bromo-*tert.*-butyl ester (Aldrich and Beckwith), A., i, 77.
  ethenyl ester (Hess and Uibrig), A., i, 319.
  ethyl ester, viscosity of the system stannic chloride and (Kurnakov, Perlmutter, and Kanov), A., ii, 360.
  mercaptan esters of (Faber and Reid), A., i, 626.
  methoxymethyl ester (Clark, Cox, and Mack), A., i, 316.
  methyl ester, effect of sucrose on the hydrolysis of (Griffith, Lamble, and Lewis), T., 390; A., ii, 302.
  p-nitrobenzyl ester (Lyons and Reid), A., i, 559.
Acetic acid, detection and estimation of salts of (Curtman and Harris), A., ii, 516.
Acetic acid, *tri*chloro-, reaction between amylene and (Timofeev and Kravcov), A., ii, 134.
  bromo-, and chloro-, hydrolysis of, in alcoholic solution (Cassel), A., ii, 249.

Acetic acid, chloro-, hydroxylammonium salts (JONES and WERNER), A., i, 380.

Acetic anhydride, preparation of (DREYFUS), A., i, 194, 441.
  estimation of (RADCLIFFE and MEDOFSKI), A., ii, 397 ; (SAGE), A., ii, 398.

Acetoacetic acid, formation of, in liver in diabetes (EMBDEN and ISAAC), A., i, 496.
  intravenous injection of (WILDER), A., i, 611.
  detection of, in urine (ROSENBLOOM), A., ii, 50.
  estimation of acetone and, in urine (ENGFELDT), A., ii, 550.

Acetone, viscosity of the system, antimony trichloride and (KURNAKOV, PERLMUTTER, and KANOV), A., ii, 360.
  and air, propagation of flame in mixtures of (WHEELER and WHITAKER), T., 267 ; A., ii, 249.
  catalytic condensation and reduction of (MAILHE and DE GODON), A., i, 315.
  compounds of calcium chloride and (BAGSTER), T., 494 ; A., i, 443.
  condensation of imines with (MAYER), A., i, 144.
  condensation of pyrrole with (TSCHELINCEV and TRONOV), A., i, 91, 93.
  estimation of (HUBBARD), A., ii, 279 ; (LJUNGDAHL), A., ii, 584.
  estimation of acetoacetic acid and, in urine (ENGFELDT), A., ii, 550.

Acetone, chloro*tri*bromo- (MOORE and THOMAS), A., i, 462.

Acetone substances, estimation of, in urine (LENK), A., ii, 399.

Acetonediethylacetal, condensation of ethyl oxalate with (WISLICENUS and SCHÖLLKOPF), A., i, 700.

Acetonetetracarboxylic acid, ethyl ester (STAUDINGER and HIRZEL), A., i, 631.

4-Acetonylbenzoic acid, 3-nitro-, and its methyl ester and phenylhydrazone (BORSCHE, STACKMANN, and MAKAROFF-SEMLJANSKI), A., i, 16.

Acetonylphthalimide, γ-chloro- (GABRIEL and OHLE), A., i, 565.

Acetophenone, and bromo-, chloro-, and cyano-, crystallographical and optical constants of (AMINOFF), A., i, 143.

Acetophenone, 4-bromo-3-nitro- (BORSCHE, STACKMANN, and MAKAROFF-SEMLJANSKI), A., i, 17.
  2:3:4:6-*tetra*hydroxy-, and its phenylhydrazone (NIERENSTEIN), T., 6 ; A., i, 150.

Acetophenonepinacone, preparation of (JOHLIN), A., i, 329.

2-Acetothienone, and amino-, nitro-, and their derivatives (STEINKOPF and JAFFÉ), A., i, 278.

Aceto-*p*-toluidide, 2-amino-, 2-chloroacetyl derivative (JACOBS and HEIDELBERGER), A., i, 584.

Acetotoluidides, bromonitro-, and nitro- (KÖRNER and CONTARDI), A., i, 86.

Acetoveratrylamide, 6-bromo- (JONES and ROBINSON), T., 912.

o-**Acetoxybenzoic acid** (*acetylsalicylic acid ; aspirin*), magnesium salt (BOUVET), A., i, 650.
  analysis of (FRANÇOIS), A., ii, 224.

m-**Acetoxybenzoic acid**, *p*-nitrobenzyl ester (LYONS and REID), A., i, 559.

p-**Acetoxycinnamonitrile** (FISCHER and NOURI), A., i, 393.

p-**Acetoxycoumaronitrile** (FISCHER and NOURI), A., i, 393.

β-**Acetoxyethylidenemalonic acid**, ethyl ester (V. AUWERS and AUFFENBERG), A., i, 627.

β-**Acetoxy-α-methylstyrene** (V. AUWERS), A., i, 267.

β-**Acetoxypropylidenemalonic acid**, ethyl ester (V. AUWERS and AUFFENBERG), A., i, 627.

β-**Acetoxy-*n*-propylphthalimide** (GABRIEL and OHLE), A., i, 563.

4′-Acetoxystilbene, 2-nitro-4-cyano- (PFEIFFER, KLINKERT, and V. POLLITZER), A., i, 141.

Acetylacetonamine. See Δ^{α}-Propenyl methyl ketone, β-amino-.

Acetylacetone, (*pentane-βδ-dione*), constitution of, and chloro- (V. AUWERS and AUFFENBERG), A., i, 629.
  action of aromatic amines on (TURNER), T., 1 ; A., i, 130.
  complex compounds of iron salts, pyridine and (WEINLAND and BÄSSLER), A., i, 6.
  action of phenyl cinnamylidenemethyl ketone with (SCHOLTZ), A., i, 462.

Acetylacetonebisazobenzene-*p*-hydrazone sulphate (TRÖGER and PIOTROWSKI), A., i, 668.

Acetylacetone-2:6-dimethoxyanilide (TURNER), T., 2.

Acetylamylacetone. See η-Methylnonane-βδ-dione.

Acetylbenzoin, *p*-nitro-, reactions of (FRANCIS), T., 1041.

Acetylbrometone. See Acetic acid, *tri*bromo-*tert.*-butyl ester.

Acetyl-*l*-cystine, *di*bromo-, and *di*iodo- (ABDERHALDEN and WYBERT), A., i, 120.

- **Acetyldi-*l*-leucyl-*l*-cystine**, *di*bromo-, and *di*chloro- (ABDERHALDEN and WYBERT), A., i, 120.
- **5-Acetyl-4:7-dimethyl-2:2-diethylhydrindene**, and its semicarbazone (FREUND, FLEISCHER, and GOFFERJE), A., i, 573.
- **4-Acetyldiphenylamine**, 2-amino-, and 2-nitro- (BORSCHE, STACKMANN, and MAKAROFF-SEMLJANSKI), A., i, 17.
- **Acetylene**, ultra-violet absorption spectra of (MASSOL and FAUCON), A., ii, 188.
  - ignition of mixtures of air and (HAWARD and SASTRY), T., 841; A., ii, 527.
  - pyrogenic condensations of (MEYER and WESCHE), A., i, 313.
  - compounds of aluminium chloride and (GANGLOFF and HENDERSON), A., i, 533.
  - preparation of acetic acid and acetaldehyde from (DREYFUS), A., i, 2.
  - copper derivative, action of, on diazo-compounds (SCHARVIN and PLACHUTA), A., i, 179.
- *α*-**Acetylglutaric acid**, ethyl ester (KÜSTER and WELLER), A., i, 443.
- **Acetylhydratocantharic acid**, and its anhydride (GADAMER), A., i, 659.
- **Acetylmalonic acid**, ethyl ester, constitution of, and *α*-bromo-, and *α*-chloro-, ethyl esters (V. AUWERS and AUFFENBERG), A., i, 628.
- **1-Acetyl-3-methylpyrazole**, 5-chloro- (MICHAELIS and ROJAHN), A., i, 481.
- **6-Acetylphenoxyacetic acid**, 4-amino-, and its derivatives (JACOBS and HEIDELBERGER), A., i, 697.
- **5-Acetyl-1-phenylaziminobenzene.** See 5-Acetyl-1-phenyl-1:2:3-benzotriazole.
- **5-Acetyl-1-phenyl-1:2:3-benzotriazole**, and its derivatives (BORSCHE, STACKMANN, and MAKAROFF-SEMLJANSKI), A., i, 17.
- *α*-**Acetyl-*β*-phenylbutyric acid.** See *α*-Phenylethylacetoacetic acid.
- **Acetyl-*p*-phenylenediazoimide** (MORGAN and UPTON), T., 193; A., i, 300.
- **4-Acetylphenylmalonic acid**, 2-nitro-, methyl ester (BORSCHE, STACKMANN, and MAKAROFF-SEMLJANSKI), A., i, 17.
- **4-Acetyl-1-phenylpyrazol-5-one-3-carboxylic acid** (BENARY, REITER, and SOENDEROP), A., i, 253.
- **Acetylsalicylic acid.** See *o*-Acetoxybenzoic acid.
- **4-Acetyl-*m*-tolylmalonic acid**, 5-nitro-, ethyl ester (BORSCHE, STACKMANN, and MAKAROFF-SEMLJANSKI), A., i, 18.
- **Acid**, $C_{12}H_{16}O_3$, from polymerisation of methylchavicol (VAN ROMBURGH and VAN DER ZANDEN), A., i, 690.
  - $C_{31}H_{40}O_{15}N_2$, from molasses (STOLTZENBERG), A., i, 153.
- **Acids**, structure of (BRIGGS), T., 261; A., ii, 254.
  - effect of neutral salts on the solubility of (HENDERSON and TAYLOR), A., ii, 77.
  - dissociation of acid salts of, in aqueous solution (THOMS and SABALITSCHKA), A., i, 700.
  - catalytic action of, in lactone formation (TAYLOR and CLOSE), A., ii, 253.
  - formation of water in the combination of bases and (ZEITLER), A., ii, 463.
  - equilibrium of bases and, in the animal body (HOWLAND and MARRIOTT), A., i, 366.
  - identification of (REID), A., i, 333; (LYMAN and REID), A., i, 334; (LYONS and REID), A., i, 559.
  - estimation of, by titration (BJERRUM), A., ii, 215.
  - aliphatic, hydrates of (CHRISTIANSEN), A., ii, 404.
    - oxidation of (LEVENE and ALLEN), A., i, 3.
    - action of, with aromatic amines (DE' CONNO), A., i, 386.
    - monocarboxylic, melting-points of (TAMMANN), A., ii, 441.
    - volatile, detection and estimation of (DYER), A., ii, 157.
      - estimation of (BOEKHOUT and DE VRIES), A., ii, 50; (UPSON, PLUM, and SCHOTT; LAMB; RICHMOND), A., ii, 277.
  - aromatic, metabolism of. See Metabolism.
  - carboxylic, transformation of the azides of (CURTIUS), A., i, 635.
- **Acids**, fatty, esters of, physiological evaluation of (MÜLLER and MURCHHAUSER), A., i, 492.
    - analysis of mixtures of (TWITCHELL), A., ii, 428.
    - higher unsaturated, fusion of, with potassium hydroxide (ECKERT), A., i, 317.
    - volatile, estimation of (GILLESPIE and WALTERS), A., ii, 549.
  - *α*-halogenated ethylenic, separation of stereoisomeric (BOUGAULT), A., i, 647.
  - organic, salts of, conductivity measurements of dissociation of (THOMS and ZEHRFELD), A., i, 699.
    - reduction of metallic salts by, in presence of oxidising agents (DHAR), T., 690; A., ii, 458.

Acids, strong, catalytic activity of (Dawson and Crann), A., ii, 26.
unsaturated, formation of, in plants (Komatsu), A., i, 139.
ionisation and structure of (Derick and Kamm), A., ii, 233.
action of bromine water on (Bilmann), A., i, 378.
complex compounds of platinum and mercury with (Bilmann and Hoff), A., i, 123.
action of sodium hypochlorite on amides of (Weerman), A., i, 560.
of the sugar group, hydrazides of (Weerman), A., i, 548; (Levene and Meyer), A., i, 631.
constitution and rotatory power of phenylhydrazides of (Hudson), A., i, 318.
Acid anhydrides. See Anhydrides, acid.
Acidosis (van Slyke and Cullen; Cullen), A., i, 521; (Fitz and van Slyke), A., i, 522; (van Slyke, Stillman, and Cullen; Stillman, van Slyke, Cullen, and Fitz), A., i, 523; (van Slyke), A., ii, 422.
Aconite alkaloids (Schulze and Liebner), A., i, 470.
Acridinium salts, chromoisomerism of (Hantzsch), A., i, 708.
Acrylhydroxamic acid (Jones and Neuffer), A., i, 326.
Actinium, charged condition of the active deposits of (Henderson), A., ii, 351.
Acylsemi-carbazic acids and **-carbazides** (Bougault), A., i, 417.
Address, presidential (Scott), T., 288.
Adenine, curative properties of (Harden and Zilva), A., i, 612.
Adenine-uracil-dinucleotide, and its brucine salt (Jones and Read), A., i, 232, 233, 597.
Adipocere, composition of (Ruttan and Marshall), A., i, 364.
human (Ruttan), A., i, 495.
Adrenaline (*suprarenine; epinephrine*), estimation of (Johannessohn), A., ii, 55.
Adsorption (Rakuzin), A., ii, 72.
and ionisation (Reychler), A., ii, 233.
and diffusion (Alexander), A., ii, 242.
of odour (van Dam; Kremer), A., i, 607.
by soils (Harris), A., ii, 443.
in chemotherapeutics and immunity (Andreev), A., i, 183.
Æsculin, microchemistry and detection of (Tunmann), A., ii, 59.
Affinity (Briggs), T., 254; A., ii, 254.
chemical (Thornton), A., ii, 357.
residual (Pickering), A., ii, 528.
Air. See Atmospheric air.
d-**Alanine**, cobalt salts (Ley and Ficken), A., i, 707.
Albumin, formation of, from different sources of carbon (Bokorny), A., i, 72.
from hens' eggs, specific gravity of solutions of (Rakuzin and Flier), A., i, 232.
adsorption of (Rakuzin), A., ii, 72, 124; (Rakuzin and Braudo), A., ii, 73, 124; (Rakuzin, Flier, and Bloch), A., ii, 73.
detection of (Potjan and Steffenhagen), A., ii, 520.
detection of, in urine (Godfrin), A., ii, 59; (Eicke; Edelmann), A., ii, 110; (Aufrecht), A., ii, 227.
use of alkalis in estimating (Palet), A., ii, 555.
estimation of, colorimetrically (Autenrieth), A., ii, 400.
estimation of, in urine (Justin-Mueller; Lenk), A., ii, 555.
Ovalbumin, detection of, in urine (Godfrin), A., ii, 59.
Albuminates, alkaline, optical activity of (Rakuzin), A., i, 180.
Alchemists, Dutch (Jorissen), A., ii, 198, 529; (Holgen), A., ii, 461; (Schelenz), A., ii, 529.
Alchemy, Chinese (Holgen), A., ii, 305.
Alcohols, partition of, between water and cotton-seed oil (Wroth and Reid), A., ii, 17.
hydrates of (Christiansen), A., ii, 404.
action of oxalyl chloride on (Adams and Weeks), A., i, 4.
identification of (Reid), A., i, 455.
aromatic, action of, with aromatic compounds in presence of aluminium chloride (Huston and Friedemann), A., i, 19.
of the cholesterol series, stereoisomeric, physiological action of (Windaus), A., i, 610.
Alcoholates, molecular weight of (Willcox and Brunel), A., i, 5.
Aldehydes, formation of, in wines (Laborde), A., i, 532.
action of hydramines with (Hess, Uibrig, and Eichel), A., i, 351, 352.
condensation of ketones with (H. and P. Ryan), A., i, 348.
interaction of thiocarbamides and (Dixon and Taylor), A., i, 11.
aliphatic, identification of (Harries and Oppenheim), A., i, 210.

Aldehydes, aromatic, condensation of indoles with (Hoscher), A., i, 167.
condensation of thiobarbituric acid and (Dox and Plaisance), A., i, 53.
colour reactions of (Pooth), A., ii, 52.
unsaturated, reactions between bisulphite compounds of, and malonic acid (Nottbohm), A., i, 27.
detection of, with Braun's reagent (Rinkes), A., ii, 550.
6-Aldehydophenoxyacetic acid, 4-nitro-, and its phenylhydrazone (Jacobs and Heidelberger), A., i, 697.
Aldol, preparation of (Grünstein), A., i, 686.
Aldoses, estimation of (Bougault), A., ii, 395.
Algae of drinking water, action of copper sulphate on (Bado), A., i, 107.
marine, occurrence of iodine in (Okuda and Eto), A., i, 437.
Algic acid (Odén), A., i, 379.
Alkali albuminates, optical activity of (Rakuzin), A., i, 180.
*per*borates, preparation of (Deutsche Gold- & Silber-Scheideanstalt vorm. Roessler), A., ii, 139.
bromides, double salts of alkaline earth bromides with (Kellner), A., ii, 469.
carbonates, titration of mixtures of hydroxides and (Clarens), A., ii, 507.
hydrogen carbonates, action of, on polyhydric phenols (v. Hemmelmayr), A., i, 645.
percarbonates, preparation of (Roessler & Hasslacher Chemical Co.), A., ii, 412.
chlorides, freezing-points of mixtures of (Richards and Meldrum), A., ii, 531.
gelatinates, optical activity of (Rakuzin and Braudo), A., i, 181.
haloids, absorption of light by (Brannigan and Macbeth), A., ii, 2.
thermal dissociation of (Ephraim), A., ii, 531.
compounds of arsenious oxide and (Schreinemakers and de Baat), A., ii, 203.
double salts of silver haloids and (Shemtschushni), A., ii, 140.
hydroxides, action of iodine on (Bougault), A., ii, 368.
titration of mixtures of carbonates and (Clarens), A., ii, 507.
Alkali metals, pyridine derivatives of (Emmert), A., i, 221.
organic compounds (Schlenk and Holtz), A., i, 255.
phosphates, and their constitution (Smith), A., ii, 309.
sulphates, crystallography and isomorphism of (Tutton), A., ii, 244.
double sulphates, containing water of crystallisation (Ephraim and Wagner), A., ii, 534.
polysulphides (Thomas and Rule), T., 1063.
Alkalis, estimation of, by titration (Bjerrum), A., ii, 215.
estimation of, with oxalic acid (Bruhns), A., ii, 270.
Alkali-blue, fate of, in the organism (Kuriyama), A., i, 70.
Alkaline earth bromides, double salts of alkali bromides with (Kellner), A., ii, 469.
carbonates, temperatures of formation and decomposition of (Hedvall), A., ii, 205.
chlorides, equilibria of, with hydrogen chloride and water (Milikan), A., ii, 572.
haloids, basic salts of (Milikan), A., ii, 257.
compounds of arsenious oxide and (Schreinemakers and de Baat), A., ii, 203.
hydrogen oxalates (Bruhns), A., i, 534.
sulphates, phototropic and phosphorescent properties of (Rodriguez Mourelo), A., ii, 229.
Alkaloids, phytochemical synthesis of (Robinson), T., 876; A., i, 664.
extraction of, in water (Launoy), A., ii, 553.
from aconite. See Aconite.
of the calabar bean. See Calabar bean.
cinchona. See Cinchona.
from corydalis. See Corydalis.
ipecacuanha. See Ipecacuanha.
morphine. See Morphine alkaloids.
mydriatic, detection of (Eder), A., ii, 346.
opium. See Opium alkaloids.
of the pomegranate tree (Hess), A., i, 349; (Hess and Eichel), A., i, 350.
of the Solanaceae, detection of (Anon), A., ii, 160.
detection of (Philippi), A., ii, 56; (Hankin), A., ii, 184.
detection of, microchemically (Tunmann), A., ii, 345.
estimation of, volumetrically (Dutoit and Lévy), A., ii, 225.

Alkannin, adsorption of (Rakuzin and Pekarskaja), A., i, 153.

Alkyl carbamates, action of alcoholic ammonia on (Brander), A., i, 560.

iodides, reaction of alkyl cyanides with, in presence of mercuric iodide (Hartley), A., i, 82.

reactions of mercury mercaptide nitrites with (Rây), T., 101; A., i, 194.

nitrates, compounds of thiocarbamide and (Taylor), T., 657; A., i, 514.

nitriles, reaction of alkyl iodides with, in presence of mercuric iodide (Hartley), A., i, 82.

nitrites, reduction of, to amines (Neogi and Chowdhuri), T., 899; A., i, 686.

phosphates, compounds of thiocarbamide and (Taylor), T., 662; A., i, 514.

sulphates, compounds of thiocarbamide and (Taylor), T., 655; A., i, 514.

thiocyanates, compounds of thiocarbamide and (Taylor), T., 659; A., i, 514.

N-**Alkylarylamines**, preparation of (Morgan), A., i, 197.

Alkyl galactosides (Bourquelot), A., i, 379.

Alkyl glucosides, biochemical synthesis of (Bourquelot), A., i, 379.

Alkylmalonic acids, *p*-nitrobenzyl esters (Lyman and Reid), A., i, 334.

Alkyloxyaminoformyl chlorides, preparation of (Jones and Neuffer), A., i, 325.

Alkyloxyurea. See Alkyloxyaminoformyl chloride.

Alkyltoluidines, nitro-, molecular refractivities of (Jansen), A., i, 128.

Allantoin in mammalian blood (Hunter), A., i, 184.

Allotropy, Röntgen-ray experiments on (Olie and Byl), A., ii, 286.

and electromotive equilibria (Smits and Aten), A., ii, 232.

Alloxan, preparation of (Biltz and Heyn), A., i, 289.

Alloxanic acid, constitution and derivatives of (Biltz, Heyn, and Bergius), A., i, 289.

Alloxantin, colour of salts of compounds resembling (Retinger), A., i, 519.

Alloys, electrolytic deposition of (Kremann, Schadinger, and Kropsch), A., ii, 574.

resistant to sulphuric acid (Irmann), A., ii, 478.

Allyl sulphate (v. Braun and Müller), A., i, 255.

Allyl alcohol, compound of aluminium chloride and (Gangloff and Henderson), A., i, 533.

Allylammonium palladochloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.

N-**Allylbetaine**, and its salts (v. Braun and Müller), A., i, 254.

Allylcarbinol, preparation of, and its phenylurethane (Grischkevitsch-Trochimovski), A., i, 154.

Allylhippuric acid, synthesis of (Sørensen), A., i, 89.

ethyl ester (Hammarsten), A., i, 81.

Allylhomocholine, and its salts (v. Braun and Müller), A., i, 254.

3-Allyloxy-1-phenyl-4-methylurazole, tautomerism of (Johnson and Acree), A., i, 480.

2-Allylphenol, 4-amino-, and 4-nitroso- (Jacobs and Heidelberger), A., i, 696.

2-Allylphenoxyacetic acid, 4-amino-, and its acetyl derivative (Jacobs and Heidelberger), A., i, 696.

1-Allylpyrrolidine, and its salts (v. Braun and Müller), A., i, 255.

N-**Allylstrychnine** (v. Braun and Müller), A., i, 255.

1-Allylthalline (v. Braun and Müller), A., i, 255.

1-Allyltheobromine (v. Braun and Müller), A., i, 255.

Aloes, detection of (Beal and Okey), A., ii, 279.

Aloe-emodin, *tetra*- and *penta*-bromo- (Léger), A., i, 518.

Aloin, molecular weight of, and its oxidation products (Seel and Kelber), A., i, 41; (Seel, Kelber, and Scharf), A., i, 577.

Aloins (Léger), A., i, 276.

Alpinia nutans, constituents of leaves of (Kafuku), A., i, 576.

Aluminium, preparation of, electrolytically (Seligman), A., ii, 414.

specific heat of (Brislee), A., ii, 475.

reduction by means of (Eckert and Pollak), A., i, 345.

action of acetic acid on (Seligmann and Williams), A., ii, 317.

Aluminium alloys, analysis of (Stansbie), A., ii, 510.

with glucinum (Oesterheld), A., ii, 89.

Aluminium salts, recovery of, from mineral silicates (Frazer, Holland, and Miller), A., ii, 570.

astringent action of (Loewy and Wolffenstein), A., i, 497.

- **Aluminium** bromide, benzenesulphinic acid compounds with (Olivier), A., i, 550.
  - carbide, preparation, properties and analysis of (Ruff and Jellinek), A., ii, 92.
  - chloride, dialysis of, and preparation of the hydrated oxide (Neidle and Barab), A., ii, 262.
    - compounds of, with unsaturated organic compounds (Gangloff and Henderson), A., i, 533.
  - hydroxide, solubility of, in ammonia and ammonium salts (Archibald and Habasian), A., ii, 93.
    - absorption of albumin by (Rakuzin and Braudo), A., ii, 73, 124; (Rakuzin, Flier, and Bloch), A., ii, 73; (Rakuzin), A., ii, 124.
    - adsorption of toxins and anti-toxins by (Rakuzin and Flier), A., i, 181, 427.
    - effect of ingestion of, on growth (Leary and Sheib), A., i, 493.
  - oxide (*alumina*), mixtures of ferric oxide and (Scheetz), A., ii, 574.
    - efficiency of, as a desiccating agent (Dover and Marden), A., ii, 500.
- **Aluminium estimation and separation:**—
  - estimation of (Berg), A., ii, 220.
  - separation of iron and (Palkin), A., ii, 581.
- **Aluminium dust,** analysis of (Clennell), A., ii, 335.
- **Alunite** from Marysvale, Utah (Butler and Gale), A., ii, 490.
- **Amalgams.** See Mercury alloys.
- *Ambrosia artemisifolia* (ragweed), constituents of pollen of (Heyl), A., i, 618.
- **Amides,** preparation of (McMaster and Langreck), A., i, 334.
  - pyrogenetic decomposition of (Boehner and Andrews), A., i, 10; (Boehner and Ward), A., i, 11.
- **Amidines,** synthesis of (Adams and Beebe), A., i, 96.
  - formation of (Knorr), A., i, 255.
- *p*-**Amidosulphobenzoic acid,** *p*-*di*chloro-, and its use in sterilisation of water (Dakin and Dunham), A., i, 433.
- **Amines** (Johnson and Bailey), A., i, 9; (Shepard), A., i, 19.
  - catalytic decomposition of (Sabatier and Gaudion), A., i, 553.
  - condensation of formaldehyde with (Kroneberg), A., i, 170.
  - formation of nitriles from (Sabatier and Gaudion), A., ii, 460; (Mailhe and de Godon), A., i, 686.
- **Amines,** aliphatic, formation of, from nitrites (Neogi and Chowdhuri), T., 899; A., i, 686.
    - action of, on phenazthionium salts (Kehrmann, Robert, and Sandoz), A., i, 226.
  - aromatic, catalytic preparation of (Badische Anilin- & Soda-Fabrik), A., i, 127.
    - mechanism of hydrolysis of (Franzen and Kempf), A., i, 262.
    - action of, on aliphatic acids (de' Conno), A., i, 386.
    - action of, on acetylacetone and benzoylacetone (Turner), T., 1; A., i, 130.
    - action of formaldehyde on (Lepetit and Maimeri), A., i, 452.
    - action of formaldehyde and sulphites on, and their derivatives (Lepetit), A., i, 197.
- **Amino-acids,** synthesis of (Hammarsten), A., i, 81; (Sørensen), A., i, 89.
  - optical properties of salts of (Ley and Ficken), A., i, 706.
  - derivatives of (Bornwater), A., i, 137.
  - compounds of ammonia and (Bergell), A., i, 448.
  - oxidation of, by chloramine-T (Dakin), A., i, 542.
  - action of, on reducing sugars (Maillard), A., i, 251.
  - substituted, titration of formaldehyde with (Clementi), A., ii, 344.
  - cyclic, methylation of (Hess and Leibbrandt), A., i, 354.
  - colorations produced by bacteria with (Cornish and Williams), A., i, 613.
  - removal and replacement of, in diet (Ackroyd and Hopkins), A., i, 237; (Geiling), A., i, 605.
  - estimation of, by the copper method (Kober), A., ii, 398.
  - estimation of, in blood (Amann), A., ii, 54.
- *α*-**Amino-acids,** formulæ of (Waterman), A., i, 631.
- **Amino-alcohols,** secondary, alkylation of (Hess, Uibrig, and Eichel), A., i, 351.
- **Amino-compounds,** preparation of (Jacobs and Heidelberger), A., i, 559.
  - aromatic, acylation of (Jacobs and Heidelberger), A., i, 552.
- **Aminohydroxy-compounds,** aromatic, electrolytic preparation of (Soc. Chim. Ind., Basle), A., i, 197.
- *β*-**Amino-ketones,** preparation and properties of (Mayer), A., i, 89.

δ-**Amino-ketones**, preparation of (Haller and Ramart-Lucas), A., i, 665.

Ammines, metallic (Ephraim and Millmann), A., ii, 319.

Ammonia, synthesis of (Le Chatelier), A., ii, 257.
  synthesis of, and its oxidation to nitric acid (Maxted), A., ii, 465.
  structure of (Briggs), T., 260 ; A., ii, 254.
  thermodynamic constants of (Keyes and Babcock), A., ii, 440.
  adsorption of, by charcoal (Richardson), A., ii, 526.
  flame produced by combustion of, in oxygen (Hammick), A., ii, 85.
  catalytic oxidation of (Andersen), A., ii, 138.
  analysis of gases used and produced in the oxidation of (Fox), A., ii, 503.
  compounds of amino-acids and (Bergell), A., i, 448.
  action of calcium and, on benzene (Dumanski and Zvereva), A., i, 124.
  action of chlorine with (Bray and Dowell), A., ii, 307.
  reactions between ammonium thiosulphate and polythionate, sulphur dioxide and (Espenhahn), A., ii, 310.
  compounds of, with platinous nitrite (Tschugaev and Kiltinovic), A., ii, 96.
  compounds of silver salts, with (Bruni and Levi), A., ii, 470.
  effect of carbohydrates on the accumulation of, by micro-organisms (Waksman), A., i, 613.
  formation of, in soils (Koch), A., i, 622.
  amount of, in blood (Henriques and Christiansen ; Barnett and Addis), A., i, 491.
  estimation of, by the boric acid method (Adler), A., ii, 40.
  estimation of, by means of formaldehyde (van Bers), A., ii, 578.
  estimation of, in blood (Henriques and Christiansen), A., i, 425.
  estimation of, in human blood (Barnett), A., i, 359.
  estimation of, in soils (Münter), A., i, 722 ; (Baragiola and Schuppli), A., ii, 380.
  estimation of, in urine (Weiss), A., ii, 217 ; (Folin and Bell), A., ii, 268.

Ammonification and nitrification in soils (Lipman and Burgess), A., i, 243 ; (Miyake), A., i, 244, 718 ; (Gainey), A., i, 721 ; (Münter), A., i, 722.

Ammonium bases, substituted, double haloids of bismuth, copper, lead, mercury and silver with (Datta and Sen), A., i, 323.

Ammonium salts, structure of (Briggs), T., 260 ; A., ii, 254.
  absorption of, by soils (Miyake), A., i, 247.
  manurial experiments with (Söderbaum), A., i, 192.
  analysis of (Moir), A., ii, 386.

Ammonium dihydrogen arsenates and phosphates, crystal structure of (W. and D. Asch), A., ii, 449.
  chloride, interaction of formaldehyde with (Werner), T., 844 ; A., i, 632.
  haloids, allotropy of (Scheffer), A., ii, 207.
  iodide, crystalline structure of (Vegard), A., ii, 296.
  molybdate, recovery of, from residues obtained in estimation of phosphorus (Friedrich), A., ii, 536.
  nitrate, polymorphism of (Wallerant), A., ii, 470.
  phosphomolybdate, occlusion of iron in (Archibald and Keegan), A., ii, 95.
  Triammonium hydrogen plumbofluoride (Ruff and Plato), A., ii, 202.
  nickel selenate (Tutton), A., ii, 415.
  silicate (Schwarz), A., ii, 31.
  sulphate, availability of, for soils (Allison and Cook), A., i, 621 ; (Wolkoff), A., i, 622 ; (Cook and Allison), A., i, 623.
  iron alum, hydrolysis of (Rae), A., ii, 94.
  *mono*sulphide, action of mercuric sulphide with (Christensen), A., ii, 33.
  polythionate, reactions between ammonium thiosulphate, sulphur dioxide, ammonia, and (Espenhahn), A., ii, 310.
  thiosulphate, reactions between ammonium polythionate, sulphur dioxide, ammonia and (Espenhahn), A., ii, 310.

Ampelopsidin (Willstätter and Zollinger), A., i, 48.

Ampelopsin, and its salts (Willstätter and Zollinger), A., i, 48.

Amygdalin, constitution of (Bau), A., i, 407.
  influence of, on the growth of *Aspergillus niger* (Waterman), A., i, 502, 530.

Amylacetoacetic acid, ethyl and menthyl esters (Rupe and Wild), A., i, 538.

Amylacetone. See ε-Methylheptan-β-one.
*iso***Amyl alcohol**, solubility of metallic salts in (Curtis and Burns), A., ii, 260.
*iso***Amylammonium** palladi- and palladochlorides (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.
Amylase, acceleration of the action of (Rockwood), A., i, 358.
  inhibition of the action of (Chrzaszcz and Joscht), A., i, 423.
  of malt, effect of bromides on action of (Thomas), A., i, 598.
   hydrolysis of starch by (Sherman and Walker), A., i, 597.
Amylene, reaction between trichloroacetic acid and (Timofeev and Kravcov), A., ii, 134.
β-*iso***Amylene**, compounds of aluminium and ferric chlorides and (Gangloff and Henderson), A., i, 533.
*iso***Amyloxyacetic acid**, ethyl ester, hydrazide of, and its derivatives (Curtius and van der Laan), A., i, 636.
*iso***Amyloxyacetylazide** (Curtius and van der Laan), A., i, 636.
*iso***Amyloxydihydroberberine** (G. M. and R. Robinson), T., 968.
*iso***Amylparabanic acid** (Stieger), A., i, 172.
1-Amylpyrrolidine, and its salts (v. Braun), A., i, 170.
3-*iso***Amylrhodanine**, preparation and derivatives of (Stieger), A., i, 171.
*iso***Amylthioparabanic acid**, and its imide (Stieger), A., i, 172.
*iso***Amylurethane** (Odaira), A., i, 81.
Anæmia, lipoids in blood in (Bloor and MacPherson), A., i, 609.
Anæsthesine, condensations of, with isethionic acid (Salkowski), A., i, 305.
Anæsthetics, detection of (Hankin), A., ii, 184.
Analysis, application of acid and alkaline reactions to (Bjerrum), A., ii, 215.
  replacement of acetic acid as a reagent in (Bäck), A., ii, 520.
  colorimetric (Le Roy), A., ii, 418.
  electrolytic (Gooch and Kobayashi; Gewecke), A., ii, 334.
  electro-volumetric, apparatus for (Kelley, Adams, and Wiley), A., ii, 512.
  microchemical (Denigès; Tunmann), A., ii, 345; (Wise; Almström), A., i, 541.
  microscopic qualitative, use of textile fibres in (Chamot and Cole), A., ii, 576.
Analytical chemistry, modern, advance in (Chapman), T., 203; A., ii, 266.
Anhydride, $C_{19}H_{13}O_4Br$, from α-bromocinnamic acid and benzoylacrylic acid (Bougault), A., i, 270.
Anhydrides, acid, aliphatic, preparation of (Dreyfus), A., i, 2.
Anhydrite, "principal" (Rózsa), A., ii, 214.
Anhydro-arabino-galactose-methoxy-tetragalacturonic acid (Ehrlich), A., i, 323.
Anhydroberberineacetophenone (G. M. and R. Robinson), T., 968.
Anhydroberberinenitromethane (G. M. and R. Robinson), T., 968.
Anhydrobisdiketohydrindene. See Bindone.
Anhydromethylenecitric acid, sodium salt. See Citarine.
Anhydromethyltetrahydrocryptopine (Perkin), A., i, 280.
Anhydrosedoheptose, and its benzylidene derivative (La Forge and Hudson), A., i, 444.
Anhydroximes (Rose and Scott), A., i, 354.
Aniline, preparation of, from ammonia and benzene (Wibaut), A., i, 386.
  regeneration of, from substituted anilines (Sabatier and Gaudion), A., i, 553.
  equilibrium of mixtures of hexane and (Keyes and Hildebrand), A., ii, 565.
  equilibrium in the system, phenol and (Voano), A., ii, 81.
  additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 207.
  action of methyl sulphate on (Sheppard), A., i, 19.
  estimation of, colorimetrically (Elvove), A., ii, 584.
Aniline, *di*bromoiodo- derivatives (Sudborough and Lakhumalani), T., 47; A., i, 128.
  p-iodo-, chloroacetyl derivative (Jacobs and Heidelberger), A., i, 552.
  nitro-, refractivity of (Jansen), A., ii, 401.
Anilinium palladochlorides, bromo-, chloro-, and nitro- (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.
2-Anilino-1-benzsulphonazole (Schrader), A., i, 709.
2-Anilinodiphenyl, 3:5-*di*nitro- (Borsche and Scholten), A., i, 390.
3-Anilinoflavinduline, 2-amino-, and its salts (Kehrmann and Weilenmann), A., i, 416.

β-Anilino-β-o-hydroxyphenylethyl ethyl ketone, and its derivatives (Mayer), A., i, 90.

Anilinomethanesulphonic acids, *p*-amino-, acetyl derivative, and *p*-chloro-, and their salts (Lepetit), A., i, 198.

1-Anilino-4-methoxy-2-methylbenzophenonesulphone (Ullmann and v. Glenck), A., i, 162.

1-Anilino-4-methoxy-2-methylthioxanthone (Ullmann and v. Glenck), A., i, 161.

1-Anilino-4-methylthioxanthone (Ullmann and v. Glenck), A., i, 160.

3-Anilino-1:8-naphthasultam-4-quinone (Zincke and Schürmann), A., i, 38.

β-Anilino-α-phenylacrylic acid, methyl ester (Wislicenus, Börner, Kurtz, and Bilhuber), A., i, 268.

β-Anilino-β-phenylpropionic acid, lactam of (Staudinger and Endle), A., i, 650.

5-Anilino-ψ-uric acid (Biltz and Heyn), A., i, 288.

Anilinoveratrole, *di*nitro- (Hindmarsh, Knight, and Robinson), T., 944.

Animal membranes, action of salts on swelling of, and of powdered colloids (Loeb), A., ii, 453.

Animal tissues, concentration of dextrose in (Palmer), A., i, 494.

Animals, emission of light by (Trojan), A., i, 427.

formation of thiocyanic acid in (Dezani), A., i, 676.

Anisic acid, *p*-nitrobenzyl ester (Lyons and Reid), A., i, 559.

p-Anisidinomethanesulphonic acid, sodium salt (Lepetit), A., i, 198.

Anisoles, *di*chloro- (Holleman), A., i, 556.

2-p-Anisoylbenzoic acid, 3:4:5:6-*tetra*chloro-, and its salts (Orndorff and Murray), A., i, 339.

Anisoylbenzylketoxime (Jörlander), A., i, 343.

Anisoylphenylethyl alcohols, β-chloro- (Jörlander), A., i, 222.

Anisoylphenylethylene glycol diacetate (Jörlander), A., i, 344.

Anisoylphenylethylene oxide (Jörlander), A., i, 222, 343.

Anisyl benzyl diketone, and its derivatives (Jörlander), A., i, 343.

Anisylbenzylglyoxal. See Anisyl benzyl diketone.

3-Anisyl-2-benzylquinoxaline (Jörlander), A., i, 343.

4-Anisylhydantoin-1-acetic acid, and its ethyl ester (Johnson and Hahn), A., i, 476.

Anisyl α-hydroxystyryl ketone (Jörlander), A., i, 343.

o-Anisylidenediacetophenone (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 208.

4-Anisylidenehydantoin-1-acetic acid, and its ethyl ester (Johnson and Hahn), A., i, 476.

α-Anisylidene-ε-methylheptan-β-one (Rupe and Wild), A., i, 539.

2-Anisylindone, and its 3-acetyl derivative (Jörlander), A., i, 344.

Anisyl β-phenylethyl ketone (Jörlander), A., i, 343.

2-Anisyl-6-phenylpyryl ferrichloride (Dilthey), A., i, 661.

p-Anisyl styryl ketone, additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 208.

Annual General Meeting, T., 273.

Anorthite, equilibrium of forsterite, silica and (Boeke), A., ii, 147.

Antagonism, dynamical theory of (Osterhout), A., i, 434, 435.

of ions in solution (Feenstra), A., i, 105.

Anthocyanins (Willstätter and Bolton), A., i, 42, 43; (Willstätter and Burdick), A., i, 44, 49; (Willstätter and Zollinger), A., i, 45, 47; (Willstätter and Weil), A., i, 46, 49.

Anthranilic acid, *p*-nitrobenzyl ester (Reid), A., i, 334.

1-Anthranilo-4-methylbenzophenonesulphone (Ullmann and v. Glenck), A., i, 162.

Anthraquinone derivatives, reduction of, by means of aluminium powder (Eckert and Pollak), A., i, 345.

Anthraquinone, 2-amino-, preparation of, and its derivatives (Farbenfabriken vorm. F. Bayer & Co.), A., i, 463.

bromo-α-hydroxy- derivatives, preparation of (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 40.

hydroxy- derivatives, preparation of benzoyl derivatives of (Wedekind & Co.), A., i, 464.

Anthraquinone colouring matters, polyhydroxy-, absorption spectra of (Meek), T., 969; A., ii, 558.

Anthraquinone-2-aldehyde, preparation of (Chemische Fabrik Griesheim Elektron), A., i, 40.

Anthraquinone-1-arsenoxide (Benda), A., i, 600.

Anthraquinonearsinic acids, and 4-amino-, 3-amino-4-hydroxy-, 4-hydroxy-, and 3-nitro-4-hydroxy-, and their derivatives (Benda), A., i, 599.

- **Anthraquinone-1:4-bisdiazonium** chloride (Schaarschmidt), A., i, 180.
- **Anthraquinone-1:5-diarsinic acid,** *di*amino*di*hydroxy-, *di*hydroxy-, and *di*nitro*di*hydroxy-, and their salts (Benda), A., i, 601.
- **Anthraquinone-1-diazonium** bromide and chloride, and 4-chloro- (Schaarschmidt), A., i, 179.
- **Anthraquinone-2:7-disulphonic acid,** sodium salt, hydrate of (Crossley), A., i, 346.
- **Anthrarufindiarsinic acid.** See Anthraquinonediarsinic acid, *di*hydroxy-.
- **Antimony,** colloidal, preparation of (Gutbier and Kräutle), A., ii, 299.
- **Antimony** *tri*chloride, viscosity of systems ethyl ether or acetone with (Kurnakov, Perlmutter, and Kanov), A., ii, 360.
    - compound of thiocarbamide and (Vanino and Mussgnug), A., i, 196.
  - sulphide, equilibrium of cuprous sulphide and (Chikashige and Yamauchi), A., ii, 143.
- **Antimony estimation and separation:—**
  - estimation of, in alloys (Hagmaier), A., ii, 181.
  - estimation of, in antimonial lead (McCabe), A., ii, 333.
  - estimation of, and its separation from tin (Prim), A., ii, 392.
  - estimation of copper, lead and (Howden), A., ii, 580.
- **Antipyrine** (1-*phenyl*-2:3-*dimethyl*-5-*pyrazolone*) and iodo-, periodides of (Emery and Palkin), A., i, 54.
  - estimation of (François), A., ii, 226; (Bougault), A., ii, 344.
- **Antiseptics,** new (Browning, Gulbransen, Kennaway, and Thornton), A., i, 240.
  - treatment of soils with (du Buisson), A., i, 529.
- **Apatite** from Sunk, Styria (Grosspietsch), A., ii, 489.
- **Aphrosiderite** from British Columbia (Larsen and Steiger), A., ii, 148.
- **Apples,** sugars in the juice of (Eoff), A., i, 531.
- **Arabinose,** kinetics of conversion of, into furfuraldehyde (Kremann and Klein), A., ii, 251.
- *l*-**Arabinose-*p*-tolylhydrazone** (van der Haar), A., i, 380.
- *l*-**Arabonamide** (Weerman), A., i, 546.
- *l*-**Arabonic hydrazide** (Weerman), A., i, 548.
- *Arachis hypogæa* (peanut), proteins of (Johns and Jones), A., i, 191, 505.
- **Arachin** (Johns and Jones), A., i, 191.
- **Aracho-*p*-ethoxyanilide** (de' Conno), A., i, 388.
- **Aracho-*p*-hydroxyanilide** (de' Conno), A., i, 388.
- **Aracho-*p*-methoxyanilide** (de' Conno), A., i, 388.
- **Aracho-α-** and **-β-naphthalides** (de' Conno), A., i, 388.
- **Aracho-*p*-phenylenediamide** (de' Conno), A., i, 389.
- **Aracho-*p*-toluidide** (de' Conno), A., i, 387.
- **Aracho-*m*-xylidide** (de' Conno), A., i, 387.
- **Arduinite** (Billows), A., ii, 492.
- **Arginase,** occurrence and activity of (Edlbacher), A., i, 670.
  - formation of urea by (Clementi), A., i, 358.
  - detection of, with formaldehyde (Clementi), A., ii, 400.
- **Arginine,** change of, into creatine in the animal body (Thompson), A., i, 369, 673; (Jansen), A., i, 606.
- **Arginine,** estimation of, in proteins (Jansen), A., ii, 184.
- **Argon,** spectrum of (Meissner), A., ii, 61.
  - dilatability and internal pressure of (Leduc), A., ii, 356.
  - estimation of, in mixed gases (Brandt), A., ii, 384.
  - apparatus for estimation of (Sieverts and Brandt), A., ii, 103.
- **Arsanilic acid.** See Phenylarsinic acid, *p*-amino-.
- **Arsenic,** colloidal, preparation of (Gutbier and Kräutle), A., ii, 298.
  - effect of, in brass (Smalley), A., ii, 315.
  - excretion of, in human urine (Lockemann), A., i, 495.
  - **Arsenious** oxide, compounds of metallic haloids and (Schreinemakers and de Baat), A., ii, 173, 203.
  - **Perarsenates,** preparation of (Aschkenasi), A., ii, 467.
  - *tri*sulphide, apparatus for extraction of sulphur from (v. Spallart), A., ii, 102.
- **Arsenic organic compounds** (Farbwerke vorm. Meister, Lucius, & Brüning; Thoms), A., i, 359; (Benda), A., i, 599.
  - aromatic (Sieburg), A., i, 486.
  - with thiophen (Steinkopf), A., i, 303.
  - used in pharmacy, preparation of (Synthetic Patents Co.), A., i, 196.

Arsenic detection and estimation :
  detection of (Vuaflart), A., ii, 331.
  detection of, in tissues (Gautier and Clausmann), A., ii, 121.
  detection and estimation of, in dextrose and in sulphuric acid (Kling), A., ii, 579.
  estimation of (Klason), A., ii, 151; (Hollins), A., ii, 382; (Lehmann), A., ii, 579.
  estimation of, as trisulphide (Schmidt), A., ii, 331.
  estimation of, in beer and in dextrose (Muttelet), A., ii, 101.
  estimation of, in lead arsenate (Gray and Christie), A., ii, 102; (Scholz and Waldstein), A., ii, 422.
  estimation of, in organic compounds (Ewins), A., ii, 101.
  estimation of, in sulphuric acid (Pérégrin), A., ii, 180.
  estimation of, in urine (Klason), A., i, 186.
1:1′-Arsenoanthranol (Benda), A., i, 600.
Arsenobenzene, physico-chemical properties of derivatives of, and their transformation in the organism (Danysz), A., i, 430.
  *di*amino*di*hydroxy-, metallic derivatives of (Danysz), A., i, 599.
Arylamines, secondary, separation of, from primary arylamines (Thomas), T., 562; A., i, 451.
Arylhydroxylamines, nitroso- (Baudisch and Fürst; Baudisch and Karzeff), A., i, 330; (Baudisch and Klaus), A., i, 331.
Ascitic fluid, estimation of albumin and globulin in (Autenrieth), A., ii, 400.
Asparagine, use of alkalis in estimating (Palet), A., ii, 555.
Aspergillus niger, metabolism of (Waterman), A., i, 73.
  citric acid fermentation by (Currie), A., i, 614.
  formation of starch-like substances by (Boas), A., i, 503.
  influence of amygdalin on the growth of (Waterman), A., i, 502, 530.
  effect of potassium nitrate on fermentation by (Molliard), A., i, 73.
Aspirin. See *o*-Acetoxybenzoic acid.
Aster, anthocyanin of (Willstätter and Burdick), A., i, 44.
Aster, summer. See *Aster* and *Callistephus.*
  winter. See *Chrysanthemum.*
Asterin, and its chloride (Willstätter and Burdick), A., i, 44.

Atmospheric air, critical constants of (Kuenen and Clark), A., ii, 405.
  solubility of, in water (Coste), A., ii, 463.
  effect of combustion of various substances in an enclosed volume of (Müller), A., ii, 463.
  propagation of flame in mixtures of acetone and (Wheeler and Whitaker), T., 267; A., ii, 249.
  ignition of mixtures of acetylene and (Haward and Sastry), T., 841; A., ii, 527.
  electrical ignition of mixtures of methane and (Wheeler), T., 411; A., ii, 300.
  estimation of carbon dioxide in (Higgins and Marriott), A., ii, 270.
  estimation of gasolene vapour in (Anderson), A., ii, 338.
  estimation of ozone and oxides of nitrogen in (Usher and Rao), T., 799; A., ii, 502.
  See also Nitrous air.
Atoms, structure of (Harkins), A., ii, 303; (Debye), A., ii, 434.
  structure and combination of (Noyes), A., ii, 287.
  positive nucleus of (Haas), A., ii, 528.
  varieties of (van den Broek), A., ii, 85.
  volumes of, at absolute zero (Le Bas), A., ii, 357.
Atomic numbers, relation of, to atomic weights (Durrant), A., ii, 253.
Atomic theory (Scott), T., 288; (Lorenz and Posen), A., ii, 14, 15.
Atomic volume. See Volume.
Atomic weight of bromine (Guye), A., ii, 199; (Moles; Reiman), A., ii, 200.
  of carbon (Moles; Guye), A., ii, 257.
  of hydrogen (Guye), A., ii, 412.
  of iodine (Guichard), A., ii, 201.
  of lead (Œchsner de Coninck), A., ii, 33; (Richards and Wadsworth), A., ii, 91.
  of lead isotopes (Fajans and Lembert), A., ii, 472.
  of tellurium (Stähler and Tesch), A., ii, 202.
  of yttrium (Hopkins and Balke), A., ii, 34.
  of zirconium (Venable and Bell), A., ii, 479.
Atomic weights (Chwolson), A., ii, 27; (Baxter), A., ii, 254.
  table of, T., 1002; (Guye), A., ii, 198.
  fundamental (Bilecki), A., ii, 197.
  numerical relations between (Vondráček), A., ii, 460.

Atomic weights, relation of atomic number to (Durrant), A., ii, 253.

Attraction, physico-chemical force of (Gurvitsch), A., ii, 123.

Atropine, detection of (Eder), A., ii, 346.
  estimation of (Rasmussen), A., ii, 431.

Augites from British Columbia (Warren, Allan, and Conner), A., ii, 149.
  aluminous, attempts at synthesis of (Schumoff-Deleano), A., ii, 496.

Aurin, additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 210.
  *tri*hydroxy- (Ghosh and Watson), T., 826.

Aurobismuthinite (Koenig), A., ii, 486.

Auromercaptobenzenes, preparation of (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 199.

2-Auromercaptobenzene-1-carboxylic acid, 4-amino-, sodium salt (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 199.

Autocatalysis, chemical dynamics of (v. Zawidzki), A., ii, 82; (v. Zawidzki and Staronka), A., ii, 83; (v. Zawidzki and Zaykowski), A., ii, 84.

Autoclave (Morey), A., ii, 305.
  use of glass-stoppered bottles in (Krauss), A., ii, 462.

Autolysis, influence of bile on (Bradley and Taylor), A., i, 364.

Avocado, new sugar from the pulp of (La Forge), A., i, 118.

Avogadro's hypothesis, thermodynamic proof of (del Lungo), A., ii, 68.

Azides (Wöhler and Martin), A., i, 383.
  sensitiveness of, and their detonation temperatures (Wöhler and Martin), A., ii, 466.

2-Azido-1-benzsulphonazole (Schrader), A., i, 709.

Azines, action of cyanic and thiocyanic acids on (Bailey and McPherson), A., i, 587.

Azine colouring matters (Kehrmann), A., i, 415.

Azlactone, $C_{16}H_{10}O_2NCl$, from *o*-chlorobenzaldehyde (Mauthner and Mika), A., i, 338.
  $C_{16}H_{10}O_2NBr$, from *m*-bromobenzaldehyde (Mauthner and Mika), A., i, 338.
  $C_{20}H_{13}O_2N$, from *a*-naphthaldehyde (Mauthner and Mika), A., i, 337.
  $C_{21}H_{15}O_3N$, from 2-methoxy-1-naphthaldehyde (Mauthner and Mika), A., i, 337.

Azobenzeneaminomethanesulphonic acid, sodium salt (Lepetit), A., i, 198.

Azobenzene-3:5:3′:5′-tetracarboxylic acid, and its sodium salt and methyl ester (Meyer and Wesche), A., i, 341.

2:2′-Azobenzoic acid, 6:6′-*di*chloro-, and its derivatives (Reich and Merki), A., i, 227.

Azocarboxylic acids (Angeli), A., i, 228.

Azo-colouring matters, bisulphite compounds of (Voroshcov), A., i, 300.

Azo-compounds and their salts, absorption spectra of (Kehrmann and Hempel), A., i, 593.

Azoimide, formation of (Sommer), A., ii, 30.

Azole derivatives, spectroscopy of (Rozanov), A., ii, 284.

Azoxybenzene, 2:2′-*di*hydroxy- (Baudisch and Haftka), A., i, 357.

Azoxybenzene-3:5:3′:5′-tetracarboxylic acid, and its methyl ester (Meyer and Wesche), A., i, 341.

Azoxy-compounds, hydroxy- (Baudisch), A., i, 356.

Azoxypiperonal, and its diphenylhydrazone (Robinson), T., 117; A., i, 227.

Azoxyveratraldehyde (Robinson), T., 121.

Azoxyveratrole, and 6-bromo-, and 6-*mono*- and 6:6′-*di*nitro- (Robinson), T., 114; A., i, 227.

B.

Babbit metal, analysis of (Hagmaier), A., ii, 181; (Witt), A., ii, 335.

Bacilli, paratyphus, biochemical properties of (de Graff), A., i, 306.
  tubercle, fats of (Bürger), A., i, 499.

Bacillus coli-aerogenes, differentiation of, by chemical means (Clark and Lubs), A., i, 528.

Bacillus paralacticus (Duchaček), A., i, 612.

Bacillus phenologenes, capable of producing phenol (Berthelot), A., i, 305.

Bacillus proteus vulgaris, scission of *r*-tyrosine by (Tsudji), A., i, 679.

Bacillus subtilis, scission of *r*-tyrosine by (Tsudji), A., i, 679.

Bacteria, luminous (Harvey), A., i, 365.
  nitrogenous requirements of (Gordon), A., i, 528.
  action of various, on caseinogen and amino-acids (Cornish and Williams), A., i, 613.
  action of, on histidine (Raistrick), A., i, 499.

- **Bacteria**, decomposition of polypeptides by (Otsuka), A., i, 369.
  - action of, on proteins (Robinson and Tartar), A., i, 498.
  - action of, on protein cleavage products (Sasaki), A., i, 107.
  - agglutinated, biochemical activity of (Zironi), A., i, 680.
  - killed, hydrolysis of racemic polypeptides by (Mito), A., i, 679.
  - of lucerne, effect of phosphorus compounds on (Truesdell), A., i, 242.
  - soil, effect of acids and alkalis on (Gruzit), A., i, 430.
    - effect of, on phosphates (Hopkins), A., i, 431.
    - influence of salts on (Greaves), A., i, 243.
- **Balance**, limitations of the (Blount), T., 1035.
- **Banana fly.** See *Drosophila.*
- **Barbituric acid**, preparation of derivatives of (Farbenfabriken vorm. F. Bayer & Co.), A., i, 285.
  - use of, in estimation of furfuraldehyde (Dox and Plaisance), A., ii, 53.
- **Barbituric acid**, thio-, condensation of aromatic aldehydes with (Dox and Plaisance), A., i, 53.
  - use of, in detection of ketohexoses (Plaisance), A., ii, 276.
  - use of, in estimation of furfuraldehyde (Dox and Plaisance), A., ii, 53.
- **Barium salts**, action of, on plant cells (Osterhout), A., i, 373.
- **Barium** hydroxide, glass valve to use with standard solutions of (Haynes), A., ii, 327.
  - oxide, action of silica with (Hedvall), A., ii, 205.
  - sulphate, properties of (Karaoglanow), A., ii, 387.
    - precipitation of (Weiser), A., ii, 311.
- **Barley**, effect of hydrogen- and hydroxyl-ion concentration on growth of seedlings of (Hoagland), A., i, 619.
  - enzymic hydrolysis of the furfuroids of (Baker and Hulton), T., 121; A., i, 310.
- **Base**, $C_{18}H_{20}O_2N_2$, from *p*-phenetidinomethanesulphonic acid (Lepetit), A., i, 199.
  - $C_{23}H_{38}O_3N_2$, or $C_{29}H_{38}O_2N_2$, and its salts and derivatives, from reduction of methylpsychotrine (Pyman), T., 440.
- **Bases**, structure of (Briggs), T., 261; A., ii, 254.
  - formation of water in the combination of acids and (Zeitler), A., ii, 463.
- **Bases**, equilibrium of acids and, in the animal body (Howland and Marriott), A., i, 366.
  - cyclic, Hofmann reaction with (v. Braun), A., i, 169.
  - inorganic, sparingly soluble, determination of strength of (Vesterberg), A., ii, 248.
- **ψ-Bases**, researches on (G. M. and R. Robinson), T., 958; A., i, 706.
- **Bauxite**, from Bihar, Hungary (v. Horváth), A., ii, 487.
- **Bean**, jack. See *Canavalia ensiformis.*
  - white. See *Phaseolus vulgaris.*
- **Beckmann rearrangement** (Kuhara and Watanabe; Kuhara and Ishikawa), A., i, 87.
- **Beer**, distribution of nitrogen in (Sharpe), A., i, 620.
  - estimation of arsenic in (Muttelet), A., ii, 101.
- **Beer's law**, application of, to various solvents (Stewart and Wright), T., 183; A., ii, 186.
- **Beet**, effect of sulphuric acid in soil on the growth of (Andrlík), A., i, 620.
- **Benzaldazine**, addition of cyanic acid to (Bailey and Moore), A., i, 355; (Bailey and McPherson), A., i, 587.
- **Benzaldehyde**, compound of aluminium chloride and (Gangloff and Henderson), A., i, 533.
  - condensation of methyl *iso*propyl ketone with (H. and P. Ryan), A., i, 318.
- **Benzaldehyde**, bromo- and chloronitro-, and their hydrazones (Reich and Turkus), A., i, 585.
- **Benzaldehyde-*o*-aminophenylhydrazone**, derivatives of (Franzen and v. Fürst), A., i, 58.
- **Benzaldehyde-*m*-aminophenylhydrazone**, and its derivatives (Franzen and v. Fürst), A., i, 60.
- **Benzaldehydecyanohydrin**, alkyl ethers of (Hess and Dorner), A., i, 337.
- **Benzaldehydephenylcarbamylhydrazone** (Bailey and McPherson), A., i, 587.
- **Benzaldehydephenylhydrazone**, autoxidation of, in alcohol (Busch and Kunder), A., i, 56.
- **Benzaldehyde-*p*-sulphonamide**, and its derivatives (Dakin), A., i, 543.
- **Benzamide**, *o*-amino-, chloroacetyl derivatives of (Jacobs and Heidelberger), A., i, 552.
  - *m*-amino- (Jacobs and Heidelberger), A., i, 559.
- ***m*-Benzamidosemicarbazide.** See Cryogenine.

Benzanthrone, synthesis of, and its derivatives (Schaarschmidt and Georgeacopol), A., i, 274.
p-**Benzarsine oxide.** See *p*-Carboxyphenylarsine oxide.
Benzaurin, additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 210.
Benzene, electronic formula of (Fry), A., i, 640.
thermal decomposition of (Zanetti and Egloff), A., i, 327.
viscosity of the system: stannic chloride and (Kurnakov, Perlmutter, and Kanov), A., ii, 360.
equilibrium of solution of acetic acid in (Beckmann, Liesche, and Gabel), A., ii, 564.
vapour, condensation of (Andrén), A., ii, 192.
electrochemical chlorination of (Fichter and Glantzstein), A., i, 124.
action of ammonia and calcium on (Dumanski and Zvereva), A., i, 124.
additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 207.
reaction of phthalyl chloride with (Copisarow), T., 10; A., i, 144.
effect of, on the olfactory organ (Backman), A., i, 498.
combustion of, in the human organism (Fuchs and v. Soós), A., i, 716.
derivatives, spectrochemistry of (v. Auwers), A., i, 266.
toxicity of, towards insects (Moore), A., i, 527, 678.
utilisation of, by plants (Bokorny), A., i, 682.
estimation of, in coal tar oil (Harker), A., ii, 338.
separation of toluene, xylene and, from light oils (Egloff), A., ii, 339.
Benzene, chloro-derivatives, molecular volumes of (Fry), A., i, 640.
nitro-derivatives, crystallography of (Steinmetz), A., i, 548; (Reposs1), A., i, 549.
nitro-, action of sulphuric acid on (Crossley and Ogilvie), A., i, 328.
s-*tri*nitro-, additive compounds of (Sudborough), A., i, 84; (Cadre and Sudborough), A., i, 85; (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 207.
Benzeneazoacetylacetone, phenylhydrazone of (Benary, Reiter, and Soenderop), A., i, 254.
Benzeneazodimethylacetonedicarboxylic acid, *p*-nitro-, ethyl hydrogen ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 148.
5-Benzeneazodiphenyl, 2-hydroxy- (Borsche and Scholten), A., i, 390.
Benzeneazodiphenylmethane (Busch and Kunder), A., i, 58.
2-Benzeneazo-1:5-*di*hydroxynaphthalene, 2-*o*-hydroxy- (Fischer and Bauer), A., i, 694.
Benzeneazo*di*hydroxynaphthalenes, *p*-hydroxy- (Ghosh and Watson), T., 823.
Benzeneazo-α-naphthalenediazonium chloride, *p*-chloro- (Tröger and Piotrowski), A., i, 669.
Benzeneazo-α-naphthol, *o*-amino- (Ghosh and Watson), T., 824.
Benzeneazo-β-naphthylamine, *p*-hydroxy-, and its hydrochloride (Ghosh and Watson), T., 824.
Benzeneazo-α-naphthylazoaniline, *p*-chloro- (Tröger and Piotrowski), A., i, 669.
Benzeneazo-α-naphthylazo-β-naphthol, *p*-chloro- (Tröger and Piotrowski), A., i, 669.
Benzeneazo-α-naphthyldiazosulphonic acid, *p*-chloro-, potassium salt (Tröger and Piotrowski), A., i, 669.
Benzeneazo-α-naphthylhydrazinesulphonic acid, *p*-chloro-, and its potassium salt (Tröger and Piotrowski), A., i, 669.
4-Benzeneazo-1-*p*-nitrophenyl-3:5-dimethylpyrazole, 4-*p*-nitro- (v. Auwers and Auffenberg), A., i, 629.
4-Benzeneazo-Δ^3-*cyclo*pentene-2:5-dione-1-carboxylic acid, 3-hydroxy-, ethyl ester (Wislicenus and Schöllkopf), A., i, 703.
α-Benzeneazo-Δ^{α}-propenyl methyl ketone, β-amino- (Benary, Reiter, and Soenderop), A., i, 254.
Benzenediazoniumsulphonates, hydroxy (Morgan and Tomlins), T., 503, 504; A., i, 482.
Benzenediazo-1 oxidesulphonic acids, and their salts (Morgan and Tomlins), T., 501; A., i, 481.
Benzenedisulphonic acid, separation of, from sulphuric acid (Dennis), A., i, 515.
Benzenedisulphonic acids, preparation and ionisation of (Drushel and Felty), A., i, 126.
Benzenesulphinic acid, aluminium bromide derivatives of (Olivier), A., i, 550.
Benzenesulphonic acid, preparation of (Comp. des Produits Chimiques d'Alais et de la Carmargue), A., i, 515.
esters of (Kuhara and Watanabe; Kuhara and Ishikawa), A., i, 87.

Benzenesulphonic acid, 2-amino-. See Sulphanilic acid.
Benzhydrols, *di*amino-, bromoamino-, and chloroamino- (MONTAGNE), A., i, 36, 37, 144.
Benzidine, theory of the oxidation of (WOKER), A., i, 62, 485; (MADELUNG), A., i, 285, 708.
Benzidine-2:6:2′:6′-tetracarboxylic acid (MEYER and WESCHE), A., i, 341.
α-Benzildioxime, preparation of (v. AUWERS), A., i, 572.
  use of, as a reagent for nickel (GROSSMANN and MANNHEIM), A., ii, 391.
Benzo-*tert*.-butylamide (BRANDER), A., i, 555.
Benzo-αα-diphenylethylamide (BRANDER), A., i, 555.
3:4-Benzofluorenone. See *allo*Chrysoketone.
Benzoic acid, carbamidophenyl ester, and its derivatives (JACOBS and HEIDELBERGER), A., i, 553.
  β-diethylamino-β′-phenoxy*iso*propyl ester, and its salts (PYMAN), T., 170; A., i, 305.
  ethyl ester, viscosity of the system stannic chloride and (KURNAKOV, PERLMUTTER, and KANOV), A., ii, 360.
  and bromo-, chloro-, and nitro-, *p*-nitrobenzyl esters (REID), A., i, 333.
Benzoic acid, amino-, *m*-chloroacetyl derivative of (JACOBS and HEIDELBERGER), A., i, 552.
  p-amino-, ethyl ester. See Anaesthesine.
    lactyl derivative, and its salts (SALKOWSKI), A., i, 392.
  amino-, bromo-, hydroxy-, and nitro-, *p*-nitrobenzyl esters (LYONS and REID), A., i, 559.
  amino-, and hydroxy-, catalytic hydrogenation of (HOUBEN and PFAU), A., i, 25.
    p-nitrobenzyl esters (LYMAN and REID), A., i, 334.
  2:3:4:6-*tetra*hydroxy-, and its derivatives (NIERENSTEIN), T., 5; A., i, 150.
  2:3:6-*tri*nitro- (KÖRNER and CONTARDI), A., i, 86.
  thiol-, esters of (KIMBALL and REID), A., i, 88.
Benzoic acid *p*-arsine oxide, cholesteryl and myricyl esters (SIEBURG), A., i, 487.
***o*-Benzoicsulphinide**, *p*-nitrobenzyl derivative of (LYONS and REID), A., i, 559.
Benzo-2:5-naphthyridine. See 2:5-Naphthadiazine.
Benzonitrile, 4-bromo-3-nitro-, and 3-nitro-4-amino-, and their derivatives (BORSCHE, STACKMANN, and MAKAROFF-SEMLJANSKI), A., i, 17.
Benzophenone, 4-bromo-4′-amino-, diazotisation of, in alcoholic solution (MONTAGNE), A., i, 469.
  bromoamino-, bromonitro-, chloroamino-, and chloronitro derivatives (MONTAGNE), A., i, 36, 37, 144.
  2:4:6:3′:5′-*penta*hydroxy-. See Maclurin.
Benzo-α-phenyl*iso*propylamide (BRANDER), A., i, 555.
Benzopyrones, bromination of (SIMONIS and HEROVICI), A., i, 408.
  alkali hydrolysis of (SIMONIS), A., i, 589.
***p*-Benzoquinone**, and its bromo- and chloro-derivatives, additive compounds of (PFEIFFER, JOWLEFF, FISCHER, MONTI, and MULLY), A., i, 207.
Benzotriphenylmethylamide (BRANDER), A., i, 555.
Benz*iso*oxadiazole, preparation of (GREEN and ROWE), T., 618; A., i, 519.
Benzoyl chloride, catalytic decomposition of (MAILHE and DE GODON), A., i, 137.
Benzoylacetiminoethyl ether, crystallographical and optical constants of (AMINOFF), A., i, 143.
Benzoylacetone, action of aromatic amines on (TURNER), T., 1; A., i, 130.
Benzoylacetone-*p*-bromoanilide (TURNER), T., 3; A., i, 130.
Benzoylacetone α- and -β-naphthalides (TURNER), T., 3; A., i, 130.
Benzoylacetylcinnamoylmethylamine (KNUST and MUMM), A., i, 415.
Benzoylacrylic acid, mixed anhydrides from (BOUGAULT), A., i, 270.
Benzoylalanine-*p*-arsine oxide (SIEBURG), A., i, 487.
Benzoylalanine-*p*-arsinic acid (SIEBURG), A., i, 487.
Benzoylamylacetone. See α-Phenyl-ζ-methyloctan-αγ-dione.
Benzoylaspartic acid-*p*-arsine oxide (SIEBURG), A., i, 487.
Benzoylaspartic-*p*-arsinic acid (SIEBURG), A., i, 487.
Benzoylbenzoin, *p*-nitro-, constitution and hydrolysis of (FRANCIS), T., 1043.
β-Benzoyl-γ-bromo-γ-3-bromo-4-methoxyphenylethylmalonic acid (KOHLER and CONANT), A., i, 569.
β-Benzoyl-γ-3-bromo-4-methoxyphenylethylmalonic acid, γ-hydroxy- (KOHLER and CONANT), A., i, 569.
γ-Benzoyl-β-3-bromo-4-methoxyphenylethylmalonic acid, methyl ester (KOHLER and CONANT), A., i, 568.

3-Benzoyl-2-*m*-bromo-*p*-methoxyphenyl-*cyclo*propane-1:1-dicarboxylic acid, and its methyl esters (Kohler and Conant), A., i, 568.

β-Benzoyl-γ-3-bromo-4-methoxyphenylvinylacetic acid (Kohler and Conant), A., i, 569.

β-Benzoyl-γ-3-bromo-4-methoxyphenylvinylmalonic acid, methyl ester (Kohler and Conant), A., i, 569.

Benzoyl-*p*-chlorophenylethylene oxide (Bodforss), A., i, 224.

Benzoylcinchoticine, and its derivatives (Kaufmann, Rothlin, and Brunnschweiler), A., i, 51.

Benzoyldi-*p*-bromophenylbenzylidenehydrotetrazone (Busch and Kunder), A., i, 58.

Benzoyldiphenylbenzylidenehydrotetrazone (Busch and Kunder), A., i, 57.

Benzoyl*iso*emetine (Pyman), T., 439.

γ-Benzoyl-γ-ethylhexane, ζ-amino-, and ζ-chloro- (Haller and Ramart-Lucas), A., i, 665.

Benzoylformazylbenzene (Busch and Kunder), A., i, 57.

Benzoylglutamic acid-*p*-arsine oxide (Sieburg), A., i, 487.

Benzoylglutamic-*p*-arsinic acid (Sieburg), A., i, 487.

Benzoylhydroxylamide (Bougault), A., i, 695.

Benzoyliminoacetamidoacetylglycineamide (Bergell), A., i, 448.

Benzoyliminodiacetic acid, monoamide of (Bergell), A., i, 448.

Benzoyl-leucine-*p*-arsine oxide (Sieburg), A., i, 487.

Benzoyl-leucine-*p*-arsinic acid (Sieburg), A., i, 487.

γ-Benzoyl-β-4-methoxyphenylethylmalonic acid, methyl ester (Kohler and Conant), A., i, 568.

β-Benzoyl-β-methylamyl alcohol, and its acetate (Haller and Ramart-Lucas), A., i, 665.

γ-Benzoyl-γ-methylhexane, ζ-chloro- (Haller and Ramart-Lucas), A., i, 665.

Benzoylmethylmaleinmethylimide. See 2:5-Diketo-4-benzoyl-1:3-dimethyl-2:5-dihydropyrrole.

2-Benzoylmethyl-1-methylglyoxalone (Kunst and Mumm), A., i, 415.

β-Benzoyl-β-methylpentane, ε-amino-, hydrochloride (Haller and Ramart-Lucas), A., i, 665.

1-Benzoyl-3-methylpyrazole, 5-chloro- (Michaelis and Rojahn), A., i, 481.

5-Benzoyl-1-methyluracil, 4-amino-, and its derivatives (Kunst and Mumm), A., i, 415.

o-3-Benzoyl-α-naphthylbenzoic acid. See 3-Benzoyl-1-phenylnaphthalene-*o*-carboxylic acid.

Benzoyl-1:4-naphthylenediazoimide (Morgan and Upton), T., 196; A., i, 300.

α-Benzoyl-β-*m*-nitrophenylethyl alcohol, β-chloro-, and its derivatives (Bodforss), A., i, 225.

Benzoylnitrophenylethylene oxides (Bodforss), A., i, 224.

8-Benzoyloxy-1-methyl-1:2:3:4-tetrahydroquinoline, and its hydrochloride, and 8-*p*-nitro- (Pyman), T., 171; A., i, 305.

Benzoyl-*p*-phenetidine, *p*-amino-, and *p*-nitro- (Pyman), T., 172; A., i, 305.

4-Benzoylphenylacetic acid, 2-nitro- (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 18.

Benzoylphenylalanine-*p*-arsine oxide (Sieburg), A., i, 487.

Benzoylphenylalanine-*p*-arsinic acid (Sieburg), A., i, 487.

β-Benzoyl-γ-phenyl-γ-3-bromo-4-methoxyphenylethylmalonic acid, and its methyl ester (Kohler and Conant), A., i, 570.

α-Benzoyl-β-phenyl-δ-*p*-chlorophenyl-$\Delta^{\alpha\gamma}$-butadiene, and its dioxide (Bodforss), A., i, 224.

Benzoyl-*p*-phenylenediazoimide (Morgan and Upton), T., 195; A., i, 300.

β-Benzoyl-α-phenylethyl alcohol, β-chloro- (Widman), A., i, 222.

Benzoylphenylethylene diacetate (Jörlander), A., i, 344.

Benzoylphenylethylene oxide, and its derivatives (Widman), A., i, 221.
  p-chloro-, and its diacetate (Jörlander), A., i, 345.

β-Benzoyl-γ-phenylethylmalonic acid (Kohler and Conant), A., i, 567.

Benzoylphenylhydrazinobenzaldehydephenylhydrazone (Busch and Kunder), A., i, 57.

4-Benzoylphenylmalonic acid, 2-nitro-, methyl ester (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 18.

4-Benzoyl-1-phenyl-3-methylpyrazole,
  5-amino-, hydrazone of (Michaelis and Rojahn), A., i, 481.
  bromo- and chloro-derivatives (Michaelis and Rojahn), A., i, 480.

3-Benzoyl-1-phenylnaphthalene-*o*-carboxylic acid (Schaarschmidt and Georgeacopol), A., i, 275.

α-Benzoyl-β-phenyl-δ-*p*-nitrophenyl-$\Delta^{\alpha\gamma}$-butadiene, and its dioxide (Bodforss), A., i, 224.

3-Benzoyl-2-phenyl*cyclo*propane-1-carboxylic acid (KOHLER and CONANT), A., i, 568.
3-Benzoyl-2-phenyl*cyclo*propane-1:1-dicarboxylic acid, methyl esters (KOHLER and CONANT), A., i, 566, 567.
β-Benzoyl-γ-phenylvinylmalonic acid, methyl ester (KOHLER and CONANT), A., i, 567.
Benzoyl-*p*-*iso*propylphenylethylene oxide (BODFORSS), A., i, 224.
Benzoyltyrosine-*p*-arsine oxide (SIEBURG), A., i, 487.
Benzoyltyrosine-*p*-arsinic acid (SIEBURG), A., i, 487.
Benzyl alcohol, behaviour of, in plants (CIAMICIAN and RAVENNA), A., i, 681.
  alcohols, *tert.*-amino-, and their derivatives (V. BRAUN), A., i, 174; (V. BRAUN and HEIDER), A., i, 175.
  bromide, 6-bromo-2-nitro- (REICH and TURKUS), A., i, 585.
  chloride, preparation of (CONANT), A., i, 640.
  iodide, 2:6-*di*nitro- (REICH and OGANESSIAN), A., i, 554.
  sulphide, compound of ferric chloride with (FORSTER, COOPER, and YARROW), T., 809; A., i, 646.
  sulphite (RICHTER), A., i, 24.
Benzylaniline, 6-bromo-2-nitro- (REICH and TURKUS), A., i, 585.
Benzylanilinium palladochloride (GUTBIER, FELLNER, KRÄUTER, FALCO, KRELL, SCHULZ, and WOERNLE), A., i, 541.
2-Benzyl-3-anisylquinoxaline, 2-α-chloro- (JÖRLANDER), A., i, 222.
β-Benzyl-α-3-bromo-4-methoxybenzylidenepropionic acid (KOHLER and CONANT), A., i, 569.
β-Benzylbutane (DUMESNIL), A., i, 654.
Benzylcarbamidonormorphine, *p*-amino- (V. BRAUN and KINDLER), A., i, 163.
Benzylcyanonormorphine, *p*-nitro- (V. BRAUN and KINDLER), A., i, 163.
(α)- and (β)-*o*-**Benzylene-2:2-dimethylhydrindenes** (FREUND, FLEISCHER, and STEMMER), A., i, 575.
Benzylethylammonium pallado-trichloride (GUTBIER and FELLNER), A., i, 542.
β-Benzylformhydroxamic acid, and its copper salt (JONES and SNEED), A., i, 330.
ε-Benzylheptan-δ-one-γε-dicarboxylic acid, ethyl ester (SCHROETER, KESSELER, LIESCHE, and MÜLLER), A., i, 147.
Benzylhydantoin-1-acetic acid, 4-hydroxy-, and its esters (JOHNSON and HAHN), A., i, 476.
α-Benzylideneacetylbutyric acid (H. and P. RYAN), A., i, 348.
Benzylideneaniline, 6-bromo-2-nitro- (REICH and TURKUS), A., i, 585.
Benzylideneaniline-*p*-sulphonamide (DAKIN), A., i, 544.
Benzylideneazobenzene-*p*-hydrazone salts, and chloro-, and nitro- (TRÖGER and PIOTROWSKI), A., i, 668.
Benzylidenediacetophenone disemicarbazone (DILTHEY), A., i, 579.
3:3′-Benzylidenedi-indole, *o*-amino-. See Di-3-indolyl-*o*-aminophenylmethane.
Benzylidenediketohydrindene, *p*-nitro- (KAUFFMANN and JEUTTER), A., i, 395.
Benzylidenemalonylthiocarbamide, and *o*-hydroxy-, and *o*-nitro- (DOX and PLAISANCE), A., i, 53.
α-Benzylidene-ε-methylheptan-β-one (RUPE and WILD), A., i, 538.
β-Benzylidenethiocarbimidoacetic acid, β-*m*-nitro- (STIEGER), A., i, 172.
β-Benzylidene*iso*thiohydantoic acid, β-*m*-nitro- (STIEGER), A., i, 173.
5-Benzylidene*iso*thiohydantoin, 5-*m*-nitro- (STIEGER), A., i, 173.
β-Benzyliminobutyric acid, ethyl ester, tautomerism of (RÜGHEIMER), A., i, 335.
4-Benzyl-1-methyl-1-*di*chloromethyl-$\Delta^{2:5}$-*cyclo*hexadien-4-ol (V. AUWERS), A., i, 34.
Benzylmethylpropylacetophenone (DUMESNIL), A., i, 654.
α-Benzyl-α-methylvaleric acid, and its amide (DUMESNIL), A., i, 654.
Benzylnormorphine, *p*-nitro-, and its hydrochloride (V. BRAUN and KINDLER), A., i, 163.
4-Benzyloxytoluene-3-benzylthiol, and its derivatives (ZINCKE and ARNOLD), A., i, 264.
β-Benzylpentane (DUMESNIL), A., i, 654.
δ-Benzylpentan-γ-one-βδ-dicarboxylic acid, ethyl ester (SCHROETER, KESSELER, LIESCHE, and MÜLLER), A., i, 147.
Benzylphthalimide, 2:6-*di*nitro- (REICH and OGANESSIAN), A., i, 554.
Benzyl*iso*picramic acid, *p*-nitro- (MELDOLA, FOSTER, and BRIGHTMAN), T., 553; A., i, 454.
Benzylsulphonalanine (JOHNSON and BAILEY), A., i, 10.
Benzylsulphonamide, potassium salt (JOHNSON and BAILEY), A., i, 9.
Benzylsulphonaminopropionamide (JOHNSON and BAILEY), A., i, 10.

- **Benzylsulphondinitrobenzylamides** (Johnson and Bailey), A., i, 10.
- **Benzylsulphonnitrobenzylamides** (Johnson and Bailey), A., i, 10.
- **Benzyltetramethylammonium** (Schlenk and Holtz), A., i, 262.
- 3-**Benzylthiol-*p*-cresol**, and its derivatives (Zincke and Arnold), A., i, 264.
- **Betaine**, $C_7H_{15}O_2N$, and its picrate, from methylation of α-aminobutyric acid (Komatsu), A., i, 140.
  - $C_{12}H_{17}O_2N$, and its picrate, from methylation of phenylalanine (Komatsu), A., i, 140.
  - $C_{13}H_{19}O_3N$, and its picrate, from methylation of tyrosine (Komatsu), A., i, 139.
- **Betaine**, formula of (Waterman), A., i, 631.
- **Betaines**, decomposition of, in plants (Komatsu), A., i, 139.
- **Bile**, influence of, on autolysis (Bradley and Taylor), A., i, 364.
  - influence of, on production of phenol (Dubin), A., i, 602.
- **Bile acids** (Wieland and Sorge), A., i, 685.
- **Bile pigments** (Küster), A., i, 421.
  - detection of (Kallós), A., ii, 555.
- **Bilirubin**, and its derivatives (Küster), A., i, 421.
  - diazo-reaction for (van den Bergh and Muller), A., ii, 58.
- **Binary systems**, *equilibrium in* (Kruyt and Heldermann; Voano), A., ii, 81; (Kruyt), A., ii, 133.
- **Bindenol**, anilides of (Wislicenus and Schneck), A., i, 274.
- *p*-**Bindenylaminobenzenesulphonic acid**, sodium salt (Wislicenus and Schneck), A., i, 274.
- **Bindenylaniline**, and its hydrochloride (Wislicenus and Schneck), A., i, 274.
- **Bindenylethylaniline** (Wislicenus and Schneck), A., i, 274.
- *p*-**Bindenylphenyldimethylamine** (Wislicenus and Schneck), A., i, 274.
- **Bindone**, and its derivatives (Wislicenus and Pfannenstiehl), A., i, 273; (Wislicenus and Schneck), A., i, 274.
- **Biological processes**, detection of emanations in (Schueminzký), A., i, 73.
- **Bioluminescence** (Harvey), A., i, 365; ii, 436.
  - and metabolism (Heller), A., i, 427.
- **Birch**, constituents of leaves of (Grasser), A., i, 437.
- 3:5-**Bisbenzeneazodiphenyl**, 2-hydroxy- (Borsche and Scholten), A., i, 390.
- **Bis-*p*-chlorotriphenylmethylhydrazine** (Senior), A., i, 97.
- **Biscyanamides**, hydrolysis of (v. Braun), A., i, 173.
- **Bis-diphenylglycollohydrazide** (Curtius and Goldberg), A., i, 637.
- **Bismuth**, enantiotropy of (Würschmidt), A., ii, 323.
  - crystalline structure of (Johnsen), A., ii, 143.
  - purification of (Mylius and Groschuff), A., ii, 37.
- **Bismuth alloys** with tin (Bucher), A., ii, 211.
- **Bismuth** *tri*chloride, double salts of, with chlorides of bivalent metals (Weinland, Alber, and Schweiger), A., ii, 374.
  - *tri*oxide, equilibrium of hydrochloric acid and (Jacobs), A., ii, 176.
  - oxychlorate (Vanino and Mussgnug), A., ii, 264.
- **Bismuth organic compounds:—**
  - haloids, compounds of thiocarbamides and (Vanino and Mussgnug), A., i, 196.
  - compounds of, with haloids of substituted ammonium bases (Datta and Sen), A., i, 323.
- **Bisthiophenylpropiol-*p*-toluidide** (Worrall), A., i, 336.
- *sym*-**Bistriarylmethylhydrazines**, molecular rearrangement of (Stieglitz and Senior), A., i, 97.
- **Bixin** (Heiduschka and Panzer), A., i, 408; (Rinkes and van Hasselt), A., i, 660.
  - constitution of (Herzig and Faltis), A., i, 577.
- **Blood**, human, determination of total volume of (de Crinis), A., i, 489.
  - hydrion concentration of (Porges), A., i, 64; (Hasselbalch), A., i, 490.
  - hydrogen number and oxygen-combining capacity of (Hasselbalch), A., i, 601.
  - of infants, acidosis in (Hasselbalch), A., i, 425.
  - mammalian, allantoin in (Hunter), A., i, 184.
  - ammonia content of (Henriques and Christiansen; Barnett and Addis), A., i, 491.
  - human, calcium content of (Lyman), A., i, 491.
  - cholesterol and its esters in (Bloor and Knudson; Denis), A., i, 236.

Blood, coagulation of (Stuber and Heim), A., i, 100; (Stuber and Partsch; Hekma; Howell), A., i, 101; (Resch), A., i, 303; (Hekma), A., i, 361; (Gasser), A., i, 426; (Herzfeld and Klinger), A., i, 671; (Chió), A., i, 672.
  chemistry of the colouring matter of (Zaleski), A., i, 485.
  relation between the dextrose concentration and the water in (Hiller and Mosenthal), A., i, 99.
  effect of the pancreas on dextrose in (v. Körösy), A., i, 714.
  diastatic activity of, in diabetes and nephritis (Myers and Killian), A., i, 369.
  enzymes of (Satta), A., i, 100.
  gases of, Barcroft's apparatus for measuring (Münzer and Neumann), A., i, 520.
  formation of lactic acid in (Macleod and Hoover), A., i, 426.
  lipoids in, in anaemia (Bloor and MacPherson), A., i, 609.
  amino-acid nitrogen in (Bock), A., i, 360.
  of fish, non-protein nitrogen in (Wilson and Adolph), A., i, 360.
  change in the residual nitrogen of, during an army march (Feigl, Knack, and Koopmann), A., i, 64.
  removal of protein and estimation of creatine in (Greenwald), A., i, 523.
  reducing power of (Feigl), A., i, 426; (Griesbach and Strassner), A., i, 491.
  sugar in (McDanell and Underhill; McGuigan), A., i, 359.
  from the liver, polysaccharide in (Macleod), A., i, 524.
  effect of carbon dioxide on the exchange of sulphates between corpuscles and plasma in (de Boer), A., i, 671.
  urea in, due to diet of oats (Lewis and Karr), A., i, 100.
  of new-born children, uric acid in (Kingsbury and Sedgwick), A., i, 601.

Blood detection and estimation:—
  detection of (Fuld), A., ii, 228.
  detection of, in urine, fæces and pathological fluids (Thevenon and Rolland; Justin-Mueller), A., ii, 432.
  detection of picric acid in (Tixier), A., ii, 584.
  estimation of ammonia in (Henriques and Christiansen), A., i, 425.

Blood detection and estimation:
  human, estimation of ammonia in (Barnett), A., i, 359.
  estimation of calcium in (Lyman), A., ii, 271.
  estimation of carbon monoxide in (Zuntz), A., ii, 384.
  estimation of chlorides in (Foster), A., ii, 539.
  estimation of cholesterol in (Bloor), A., ii, 275.
  estimation of creatine and creatinine in (Wilson and Plass), A., i, 360.
  estimation of creatinine in (Gettler and Oppenheimer), A., ii, 184.
  estimation of dextrose in (Schumm), A., i, 713; (Bauzil and Boyer; McGuigan and Ross), A., ii, 548.
  estimation of amino-nitrogen in (Bock), A., ii, 159.
  estimation of oxygen in (van Slyke), A., ii, 328.
  estimation of polypeptides and amino-acids in (Amann), A., ii, 54.
  estimation of sugar in (Feigl), A., i, 64; (Rainy and Hawick), A., ii, 49; (Wolf and Ball), A., ii, 106; (Cammidge), A., ii, 276; (McGuigan), A., ii, 428.
  estimation of uric acid in (Bogert), A., ii, 518.

Blood-corpuscles, glycolytic enzymes of (Lombroso), A., i, 182.
  red, endocoagulation in (Rohonyi), A., i, 236.
    permeability of, to electrolytes (Rohonyi; Rohonyi and Lóránt), A., i, 235.
    absorption of carbon dioxide by (Buckmaster), A., i, 671.

Blood serum, ultra-violet absorption spectra of (Lewis), A., ii, 62.
  tables for the alkaline reserve of (McClendon, Shedlov, and Thomson), A., i, 671.
  effect of phosphates on the calcium in (Binger), A., i, 677.
  human, phosphates in (Feigl), A., i, 520.
  estimation of albumin and globulin in (Autenrieth), A., ii, 400.
  estimation of chlorine in (Laudat), A., ii, 539.

Body fluids, detection of ferrous salts in (Popesco), A., ii, 44.

Boiling point, variation of, with chemical constitution in homologous series (Forbes), A., ii, 292.
  ratio of, to the critical temperature (Herz), A., ii, 14.

- **Bones**, estimation of selenium in (Gassmann), A., ii, 540.
- **Boric acid.** See under Boron.
- **Borohydrates.** See under Boron.
- **Boron**, pure, preparation of (Podszus), A., ii, 374.
  - compounds of, with hydrogen and oxygen (Travers, Gupta, and Ray), A., ii, 307.
- **Boron alloys** with iron (Tschischevsky and Herdt), A., ii, 372.
- **Boron compounds**, action of, on growth of wheat (Cook and Wilson), A., i, 721.
- **Boron** *tri*oxide, and its hydrates (Myers), T., 172; A., ii, 204.
  - **Boric acid**, estimation of, volumetrically (St. John), A., ii, 152.
    - estimation of, in glass (Nicolardot and Boudet), A., ii, 383.
  - **Borates** (Sborgi and Mecacci), A., ii, 138.
  - **Perborates**, detection of, in presence of other per-salts (Monnier), A., ii, 98.
  - **Borohydrates**, preparation, properties and constitution of (Travers, Gupta, and Ray), A., ii, 307.
- **Boron**, estimation of, in boron steel (Aschman), A., ii, 102.
- **Boron steel**, estimation of boron in (Aschman), A., ii, 102.
- **Brain**, cerebrosides of the (Levene and West), A., i, 525.
- **Brass**, effect of arsenic in (Smalley), A., ii, 315.
- **Brassidic acid**, isomerism of erucic acids and (Mascarelli), A., i, 195.
- **Braun's reagent**, use of (Rinkes), A., ii, 550.
- **Brazilin**, constitution of (Pfeiffer and Grimmer), A., i, 661.
- **Bread**, digestibility of (Blake), A., i, 361.
- **Brilliant-green** (Browning, Gulbransen, Kennaway, and Thornton), A., i, 240.
- **Bromination** (Datta and Chatterjee), A., i, 15.
- **Bromine**, atomic weight of (Guye), A., ii, 199; (Moles; Reiman), A., ii, 200.
  - free energy of various forms of (Lewis and Randall), A., ii, 15.
  - mixture of chlorine and, as a quantitative light-filter (Peskov), A., ii, 349.
  - determination of molecular weights in (Wright), A., ii, 28.
  - apparatus for recovery of (Collings), A., ii, 29.
  - water, action of, on ethylene (Read and Williams), T., 240; A., i, 313.
- **Bromine**:—
  - **Hydrobromic acid**, density of (Reiman), A., ii, 137, 200; (Guye), A., ii, 199; (Moles), A., ii, 200; (Murray), A., ii, 201.
  - **Bromides**, estimation of (Rupp), A., ii, 510.
    - estimation of, in presence of chlorides (Rupp and Hollatz), A., ii, 327.
- **Bromine**, estimation of, in organic compounds (Merl and Lüft), A., ii, 383.
- **Brucine**, compound of mercuric nitrite and (Rây), T., 509; A., i, 470.
- **Bucherer reaction** (Franzen and Kempf), A., i, 262.
- *n*- and *iso*-**Butaldehydes**, derivatives of (Harries and Oppenheim), A., i, 210.
- *cyclo***Butane-1:3-diones**, relationship of polymeric ketens to (Schroeter, Kesseler, Liesche, and Müller), A., i, 145.
- *a*-*sec*.-**Butoxyaminoformyl** chloride (Jones and Neuffer), A., i, 325.
- *sec*.-**Butoxyethylaminoformyl** chloride (Jones and Neuffer), A., i, 325.
- **Butter**, nutritive value of substitutes for (Halliburton and Drummond), A., i, 673.
  - estimation of stearic acid in the fat of (Holland, Reed, and Buckley), A., ii, 50.
- *iso*- and *tert*.-**Butyl** bromides, equilibrium of the dissociation and formation of (Brunel), A., i, 625.
- *sec*.-**Butyl alcohol**, condensation of *cyclo*hexanol with (Guerbet), A., i, 694.
- *tert*.-**Butylamine** nitrite (Brander), A., i, 555.
- *n*-**Butylammonium** palladi- and palladochlorides (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.
- *n*-**Butylaniline**, preparation of, and *p*-nitroso-, and their derivatives (Reilly and Hickinbottom), T., 1026.
- **Butylbenzene**, γ-chloro- (v. Braun and Neumann), A., i, 283.
- **Butylchloral** alcoholates, molecular weight of (Willcox and Brunel), A. i, 5.
- γ-**Butylene**, compound of aluminium chloride and (Gangloff and Henderson), A., i, 533.
- *iso***Butylfluorene** (Freund, Fleischer, and Stemmer), A., i, 575.
- *a*-**Butylhexoylurethane** (Odaira), A., i, 81.
- *iso***Butylxanthic acid**, cuprous salt (Montequi Díaz de Plaza), A., i, 249.

- **Butyric acid**, distillation of, in steam (RICHMOND), A., i, 316.
  - alkali salts, oxidation of, by hydrogen peroxide (COHEN and HURTLEY), A., i, 535.
  - cholesterol ester (SALKOWSKI), A., i, 716.
  - ethyl ester, viscosity of the system stannic chloride and (KURNAKOV, PERLMUTTER, and KANOV), A., ii, 360.
  - methoxymethyl ester (CLARK, COX, and MACK), A., i, 316.
  - *p*-nitrobenzyl ester (REID), A., i, 333.
  - separation and estimation of, in biological products (PHELPS and PALMER), A., ii, 278.
- **Butyric acid**, bromo-, action of sodium methoxide with (MADSEN), A., ii, 250.
  - β-hydroxy-, intravenous injection of (WILDER), A., i, 611.
    - estimation of, gravimetrically (VAN SLYKE), A., ii, 107.
    - estimation of, in urine (OHLSSON), A., ii, 51; (ENGFELDT), A., ii, 398.
  - β-iodo-αβ-thio-, silver salt (RÂY and DEY), T., 512; A., i, 442.
- **Butyric acids**, amino-, and hydroxy-, *p*-nitrobenzyl esters (LYONS and REID), A., i, 559.
- *iso***Butyrylfluorene** (FREUND, FLEISCHER, and STEMMER), A., i, 575.

C.

- **Cacao**, estimation of theobromine and caffeine in (SAVINI), A., ii, 109.
- **Cacodylic acid**, piperazine salt (ASTRUC), A., i, 9.
- **Cadmium**, allotropy of (GETMAN), A., ii, 533.
  - metallic, rate of dissolution of, in a solution of iodine (VAN NAME), A., ii, 411.
  - electroanalysis of (GUZMÁN CARRANCIO and POCH), A., ii, 509.
- **Cadmium alloys** with tin (BUCHER), A., ii, 211.
- **Cadmium** bromide and iodide, equilibrium of, with the free halogen (VAN NAME and BROWN), A., ii, 456.
  - fulminate (WÖHLER and MARTIN), A., i, 383.
  - nitrite (RÂY), T., 159; A., ii, 208.
- **Cadmium**, estimation of, and its separation from zinc (ERICSON), A., ii, 424.
- **Cæsium** chloride, melting points of, and freezing points of its mixtures with alkali chlorides (RICHARDS and MELDRUM), A., ii, 531.
- **Cæsium** chloride, double salts of, with calcium and strontium chlorides (JAMIESON), A., ii, 139.
  - germano-, plumbi-, and stanni-fluorides (SKRABAL and GRUBER), A., ii, 263.
  - nickel selenate (TUTTON), A., ii, 415.
  - dithionate, crystallographic constants of (ROSE), A., ii, 257.
- **Caffeic acid**, α-cyano-, ethyl ester (LAPWORTH and WYKES), T., 798.
- **Caffeine**, physiological effect of, and its detection in urine (HOLLANDE and THÉVENON), A., ii, 55.
  - estimation of, in cacao and chocolate (SAVINI), A., ii, 109.
- **Caffolide**, and its disilver salt (BILTZ and HEYN), A., i, 289.
- **Calabar bean**, alkaloids of (POLONOVSKI), A., i, 706.
- **Calcite**, microchemical detection of (THUGUTT), A., ii, 508.
- **Calcium**, action of ammonia and, on benzene (DUMANSKI and ZVEREVA), A., i, 124.
  - excretion of, in man (NELSON and WILLIAMS), A., i, 103; (NELSON and BURNS), A., i, 104.
  - metabolism. See Metabolism.
- **Calcium salts**, physiological action of, in plants (ROBERT), A., i, 436.
  - in human blood (LYMAN), A., i, 491.
- **Calcium**:—
  - **Tricalcium** aluminate, formation of (CAMPBELL), A., ii, 572.
- **Calcium** carbonate (SEYLER and LLOYD), T., 994; A., ii, 571.
  - solubility and precipitation of (JOHNSTON and WILLIAMSON), A., ii, 213.
  - solubility of, in boiling water (CAVAZZI), A., ii, 532.
  - chloride, double salt of cæsium chloride and (JAMIESON), A., ii, 139.
    - compounds of acetone and (BAGSTER), T., 494; A., i, 443.
    - granular, use of, as a drying agent (MCPHERSON), A., ii, 500.
  - nitrate, basic (BUSVOLD), A., ii, 207.
  - oxide (*lime*), action of silica with (HEDVALL), A., ii, 205.
  - phosphates (BASSETT), T., 620; A., ii, 413.
    - solubility of, in citric acid (RAMSAY), A., ii, 413.
  - silicate, melting point of (DOELTER), A., ii, 456.
  - sulphite, solubility of, in water and sugar solutions (VAN DER LINDEN), A., ii, 311.

Calcium detection and estimation :—
detection of, in presence of barium and strontium (KARAOGLANOW), A., ii, 383.
detection of, in plant tissues (MOLISCH), A., ii, 387.
estimation of, in blood and milk (LYMAN), A., ii, 271.
Calculations, chemical, chart for (DEMING), A., ii, 567.
Calf, efficiency of milk substitutes in feeding the (CARR, SPITZER, CALDWELL, and ANDERSON), A., i, 192.
Callistephin, and its chloride (WILLSTÄTTER and BURDICK), A., i, 44.
Callistephus, anthocyanin of (WILLSTÄTTER and BURDICK), A., i, 44.
Calorimeter (MACINNES and BRAHAM), A., ii, 560.
*pericyclo***Camphane** (BREDT and HOLZ), A., i, 656.
β-*pericyclo***Camphanol**, and its derivatives (BREDT and HOLZ), A., i, 656.
β-*pericyclo***Camphanone** (*camphenone* ; *dehydrocamphor*), and its derivatives (BREDT and HOLZ), A., i, 655.
Camphenilone, oxidation of (NAMETKIN, GREKOVA, and CHUCHRIKOVA), A., i, 151.
Camphenone. See β-*pericyclo*Camphanone.
*cyclo***Campholenic acid**, and its derivatives (BREDT and HOLZ), A., i, 656.
dl-α- and -β-**Campholides**, and their derivatives (BREDT), A., i, 561.
Camphor, physiological action of various forms of (JOACHIMOGLU), A., i, 528.
Camphoraldehydic acids, and their derivatives (BREDT), A., i, 560.
Camphoric acid, *p*-nitrobenzyl ester (LYONS and REID), A., i, 559.
semialdehyde. See Camphoraldehydic acid.
d-**Camphoric acid**, salts and esters of (THOMS and RUNZE), A., i, 699.
*cycloiso***Camphoronic acid** (BREDT and HOLZ), A., i, 657.
dl-**Camphorquinone** (BREDT), A., i, 561.
β-**Camphorylidenepropionic acid**, and its derivatives (RUPE and BURCKHARDT), A., i, 141.
Camphorylpropionic acid, β-hydroxy-, salts and lactone of (RUPE and BURCKHARDT), A., i, 142.
Canavalia ensiformis (jack-bean), proteins from (JONES and JOHNS), A., i, 191.
Canavalin (JONES and JOHNS), A., i, 191.
Cantharic acid, barium salt, pyrogenic decomposition of (GADAMER), A., i, 704.
Cantharidide (RUDOLPH), A., i, 468.
Cantharidin (GADAMER), A., i, 659, 704.
and its derivatives (RUDOLPH), A., i, 468.
*iso***Cantharidin**, constitution of (GADAMER), A., i, 659.
Caoutchouc, preparation of (OSTROMISSLENSKI), A., i, 399.
from *Eucommia ulmoides* (SIEVERS), A., i, 346.
vulcanisation of (PEACHEY), A., i, 406.
preparation of substances like ebonite, celluloid and guttapercha from (OSTROMISSLENSKI), A., i, 403.
synthesis of chlorides from (OSTROMISSLENSKI), A., i, 404.
estimation of (WESSON and KNORR), A., ii, 341.
vulcanised, estimation of sulphur in (EATON and DAY), A., ii, 150.
Capillarity (BANCROFT), A., ii, 362.
and supercooling (BIGELOW and RYKENBOER), A., ii, 444.
Capillary layer, structure of (BAKKER), A., ii, 16.
Capparis callosa, lime and silica in (MOLISCH), A., i, 505.
Caramel, chemistry of (CUNNINGHAM and DORÉE), T., 589 ; A., i, 513.
Caramelan, preparation, constitution and derivatives of (CUNNINGHAM and DORÉE), T., 593 ; A., i, 513.
Carbamic acid, thiol-, ethyl ester, acetyl derivative (KNORR), A., i, 547.
Carbamide, origin and distribution of, in nature, and its estimation (FOSSE), A., i, 73.
preparation of, from cyanamide (SCHMIDT), A., i, 688.
preparation of, by the desulphurisation of thiocarbamides (SCHMIDT), A., i, 687.
action of acetic anhydride with (WERNER), A., i, 11.
decomposition of, by nitrous acid (WERNER), T., 863 ; A., i, 639.
thio-. See Thiocarbamide.
See also Urea.
Carbamides, constitution of (WERNER), T., 863 ; A., i, 11, 639.
acylation of (JACOBS and HEIDELBERGER), A., i, 552.
thio-. See Thiocarbamides.
m-**Carbamido-oxanilamide**, and its *m*-chloroacetyl derivative (JACOBS and HEIDELBERGER), A., i, 583.
α-**Carbamido-β-phenylpropionic acid**, estimation of, in presence of urea and amino-acid (ROHDE), A., ii, 344.
Carbazole, 3-nitro-, preparation of, and its halogen derivatives (AKTIEN GESELLSCHAFT FÜR ANILINFABRIKATION), A., i, 475.

Carbazole, nitro-derivatives (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 53.
α-Carbethoxy-β-anilino-β-phenyl-α-ethylpropionic acid, and its lactam (Staudinger and Modrzejewski), A., i, 650.
Carbethoxy-3:3-dimethyl*cyclo*pentanone, cyano-. See 1:1-Dimethyl*cyclo*pentan-3-one-2-carboxylic acid, 2-cyano-, ethyl ester.
6-Carbethoxyphenoxyacetic acid, 4-nitro-, ethyl ester (Jacobs and Heidelberger), A., i, 697.
Carbohydrates, analysis of mixtures of (Kolthoff), A., ii, 223.
α-Carbomethoxy-β-anilino-αβ-diphenylpropionic acid, lactam of (Staudinger and Hirzel), A., i, 651.
Carbon, atomic weight of (Moles; Guye), A., ii, 257.
  structure of (Debye and Scherrer), A., ii, 437.
  spectra of (Rafferty), A., ii, 61.
  oxidation of, in air, and its combination with nitrogen (Lidov), A., ii, 86.
Carbon compounds, chemistry of, compared with that of silicon compounds (Stock), A., ii, 204.
Carbon *tetra*chloride, preparation of (The Dow Chemical Co.), A., i, 77.
  *sub*oxide (Diels), A., ii, 370.
    preparation of (Stock and Stoltzenberg), A., ii, 308.
  *mon*oxide, action of alkalis with (Gianoli), A., ii, 85.
    estimation of, in blood (Zuntz), A., ii, 384.
  *di*oxide, explosive potential in, at high pressure (Guye and Stanesch), A., ii, 231.
    equilibrium of, with silicon and titanium dioxides (Niggli), A., ii, 211.
    new absorbent for (Kelley), A., ii, 43.
    apparatus for absorption of (Wesson), A., ii, 332.
    adsorption of, by charcoal (Richardson), A., ii, 526.
    absorption of, by blood corpuscles (Buckmaster), A., i, 671.
    detection of minute quantities of (Haas), A., i, 433.
    estimation of, in the air (Higgins and Marriott), A., ii, 270.
    estimation of, in alveolar air and blood (Henderson and Morriss), A., ii, 506.
    estimation of, in carbonates (Zinn), A., ii, 270.
Carbon *di*oxide, estimation of, in water (Tillmans and Heublein), A., ii, 332; (van Slyke), A., ii, 422; (McClendon; Winkler), A., ii, 423.
  Carbonic acid, ionisation constants of (Seyler and Lloyd), T., 138; A., ii, 196.
    velocity of neutralisation and dissociation constant of (Thiel), A., ii, 134.
    estimation of, and its salts, volumetrically (Kolthoff), A., ii, 506.
  Carbonates (Seyler and Lloyd), T., 138, 991; A., ii, 196, 571.
    acid and normal, titration of mixtures of, and hydroxides (Claesens), A., ii, 507.
    apparatus for estimation of, in limestone (Barker), A., ii, 506.
    estimation of, in soils (Hutin), A., ii, 541.
  Percarbonates, detection of, in presence of other persalts (Monnier), A., ii, 98.
Carbon *di*sulphide, vapour pressures of mixtures of methyl alcohol and (Büchner and Prins), A., ii, 441.
  oxysulphide. See Carbonyl sulphide.
Carbon detection and estimation:—
  detection of (Müller; Minter and Haigh), A., ii, 269.
  detection of, microchemically (Emich), A., ii, 218.
  estimation of, in organic compounds (Wise), A., i, 541.
  organic, estimation of, in soils (Shorey and Fry), A., ii, 422.
    estimation of, in water (Bado), A., ii, 541.
Carbonates. See under Carbon.
Carbonyl chloride, preparation of (Plotnikov and Salatko-Petrischtsche), A., ii, 138.
    compounds of acyloxyammonium salts with (Jones and Neuffer), A., i, 325.
  sulphide (Stock and Kuss), A., ii, 205.
Carbostyril ethyl and methyl ethers, preparation of, and their picrates (Kaufmann and de Petherd), A., i, 355.
4-Carboxybenzeneazo-1:5-*di*hydroxynaphthalenes (Fischer and Bauer), A., i, 694.
3-Carboxybenzeneazo-β-naphthol, 5-chloro-4-hydroxy- and 4-hydroxy- (Meldola, Foster, and Brightman), T., 538; A., i, 454.

4-*o*- and *p*-**Carboxybenzoyl-1-phenyl-3-methylpyrazoles**, 5-chloro-, and their salts and methyl esters (MICHAELIS and ROJAHN), A., i, 481.
4-Carboxybenzyl methyl ketone, 2-nitro-. See 4-Acetonylbenzoic acid, 3-nitro-.
2-Carboxy-4-dibenzylmethylammonium-1-benzoquinone (MELDOLA, FOSTER, and BRIGHTMAN), T., 538; A., i, 453.
Carboxydisulphonic acids, preparation of (NOTTBOHM), A., i, 27.
α-**Carboxy-θ-methyldecoic acid**, and its derivatives (LEVENE and ALLEN), A., i, 3.
α-**Carboxy-ε-methylheptoic acid** (LEVENE and ALLEN), A., i, 4.
α-**Carboxy-η-methylnonoic acid** (LEVENE and ALLEN), A., i, 4.
α-**Carboxy-ζ-methyloctoic acid**, and its ethyl ester (LEVENE and ALLEN), A., i, 3.
6-Carboxyphenoxyacetic acid, 4-amino-, and 4-nitro-, and their derivatives (JACOBS and HEIDELBERGER), A., i, 697.
4-Carboxyphenylacetic acid, 2-nitro-, and its methyl ester (BORSCHE, STACKMANN, and MAKAROFF-SEMLJANSKI), A., i, 16.
p-**Carboxyphenylarsine oxide** (SIEBURG), A., i, 486.
Carixanthide (BOCQUILLON), A., i, 276.
Carnations, effect of application of fertilisers to (BEAL and MUNCIE), A., i, 190.
Carnotite, concentration of radium in (LOOMIS and SCHLUNDT), A., ii, 31.
Carolixanthide (BOCQUILLON), A., i, 276.
Carotinoids, detection of, in plants (VAN WISSELINGH), A., ii, 554.
Carvernularia haberi, bioluminescence in (HARVEY), A., i, 365.
Cascara, detection of (BEAL and OKEY), A., ii, 279.
Casein, solubility of, in solutions of sodium chloride (RYD), A., i, 301.
Caseinogen, injection and excretion of (V. AÁRON), A., i, 717.
  action of bacteria on (CORNISH and WILLIAMS), A., i, 613.
  estimation of hydrolysis of, in presence of carbohydrates (HART and SURE), A., ii, 111.
Cassiterite, crystal structure of (WILLIAMS), A., ii, 450.
Castor oil, action of nitric acid on (BRIGHTMAN), A., i, 626.
Catalase, relation between oxydase and, in plants (REED), A., i, 424.
Catalysis, studies in (GRIFFITH, LAMBLE, and LEWIS), T., 389; A., ii, 302; (LEWIS), T., 457, 1086; A., ii, 302; (DHAR), T., 690, 707; A., ii, 458.
  by acids (DAWSON and CRANN), A., ii, 26.
  contact (BANCROFT), A., ii, 566.
  heterogeneous, theory of (GURVITSCH), A., ii, 136.
  reversible (SABATIER and GAUDION), A., ii, 460.
Catalytic hydrogenation of organic compounds (BADISCHE ANILIN- & SODA-FABRIK), A., i, 377.
Catechol ethers, substituted, orientation of (JONES and ROBINSON), T., 903; A., i, 690.
    scission of (G. M. and R. ROBINSON), T., 929; A., i, 692.
  diethyl ether, 4:5-*di*nitro- (G. M. and R. ROBINSON), T., 933.
  methylene ethers, bromo-, bromonitro-, and nitroamino- (JONES and ROBINSON), T., 913.
    chloro-, chlorobromo-, and chloronitro- (ORR, ROBINSON, and WILLIAMS), T., 949.
  distinction between quinol, resorcinol and (WOLFF), A., ii, 182.
  detection of, and its distribution in plants (JOACHIMOWITZ), A., i, 682.
Cathode, palladium, occlusion of hydrogen by (SMITH and MARTIN), A., ii, 64.
Cell or Cells, electrochemical, design of, for conductivity measurements (WASHBURN), A., ii, 10.
  cadmium, specific heats of (SEIBERT, HULETT, and TAYLOR), A., ii, 231.
  conductivity, for electro-titration (ROBBINS), A., ii, 235.
  fuel (BAUR, PETERSEN, and FÜLLEMANN), A., ii, 116; (TREADWELL), A., ii, 117.
  gas detonating (TRAUTZ), A., ii, 74.
  non-aqueous, electromotive force of (NELSON and EVANS), A., ii, 232.
Cell or Cells, physiological, living, diffusion of electrolytes through (LOEB), A., i, 66, 67, 102.
    oxidation of colouring matters in (SCHLÄPFER) A., i, 187.
  permeability of (KJÖLLERFELDT), A., i, 605.
  staining of, by colouring matters (SCHULEMANN), A., i, 429.
  plant. See Plant cells.
Cellulose, volatile compounds produced in the bisulphite treatment of (KERTÉSZ), A., i, 8.
  trimethyl glucose from (DENHAM and WOODHOUSE), T., 244; A., i, 320.

Cellulose *tri*nitrate, deflagration of (Trapani), A., i, 380.
Cephæline, toxicity of derivatives of (Walters and Koch), A., i, 612; (Walters, Eckler, and Koch), A., i, 717.
  allyl ether (Lilly & Co.), A., i, 410.
  amyl ethers, preparation of (Meader), A., i, 475.
  *iso*amyl ether, and its salts (Meader), A., i, 348.
  butyl ether (Meader), A., i, 410.
  *iso*butyl and propyl ethers, and their salts (Meader), A., i, 91.
Cerebrosides (Levene and West), A., i, 525, 657; (Levene and Meyer), A., i, 657.
Cerebro-spinal fluid, human, enzymes of (Leschke and Pincussohn), A., i, 363.
Cerium alloys with iron (Vogel), A., ii, 259.
Cerium oxides, adsorption of gases by (Chase), A., ii, 475.
Chabazite from Hungary (Vendl), A., ii, 493.
Charcoal, absorption of gases by (Richardson), A., ii, 526; adsorption of sulphur dioxide by (Williams), A., ii, 362.
  animal, adsorption capacity of (Joachimoglu), A., ii, 42.
  wood, heat of combustion of (Nikitin), A., ii, 66.
"**Chelalbin**," and its derivatives (Karrer), A., i, 349.
Chelerythrine, and its derivatives (Karrer), A., i, 349.
Chemical constitution and absorption spectra of organic compounds (British Association Reports), A., ii, 435.
  and rotation of optically active compounds (Rupe and Wild), A., i, 538; (Rupe and Silberstrom), A., ii, 435.
  and electrical conductivity (Fink), A., ii, 163.
  and variation of the boiling point in homologous series (Forbes), A., ii, 292.
  relation between thermal properties and, of organic compounds (Pagliani), A., ii, 120.
  and crystal structure (Groth), A., ii, 446.
  and colour (Kauffmann), A., i, 391, 394; (Moir), A., ii, 349, 557; (Kehrmann and Hempel), A., i, 593.
  and coagulating capacity (Gann), A., ii, 21.
Chemical constitution, relation between odour and (Prins), A., i, 607.
  relation between physiological action and (Pyman), T., 167, 1103; A., i, 304.
  reactions, kinetics of (Gerasimov), A., ii, 133.
  at high temperatures (Lewis), T., 1086.
Chemotherapeutics, adsorption in (Andreev), A., i, 183.
Cherry. See *Prunus avium.*
Chestnut, edible, constituents of the leaves of (Curtius and Franzen), A., i, 438.
Chicory, degradation of inulin in the root of (Wolff and Geslin), A., i, 720.
Children, creatine excretion in (Denis, Kramer, and Minot), A., i, 526.
Chitin, chemical constitution of (Morgulis), A., i, 407.
Chloral alcoholates, molecular weight of (Willcox and Brunel), A., i, 5.
Chloral-2-acetothienoneoxime (Steinkopf and Jaffé), A., i, 278.
Chloramine-T, oxidation of amino-acids with (Dakin), A., i, 542.
Chlorates. See under Chlorine.
Chlorine, preparation of (Solvay Process Co.), A., ii, 530.
  mixture of bromine and, use of, as a quantitative light-filter (Peskov), A., ii, 349.
  action of ammonia with (Bray and Dowell), A., ii, 307.
  Hydrochloric acid, electrolysis of (Hanck), A., ii, 462; (Müller), A., ii, 463.
    equilibrium of bismuth trioxide and (Jacobs), A., ii, 176.
    generator for (Sweeney), A., ii, 568.
  Chlorides, estimation of (Kolthoff), A., ii, 379.
    estimation of, in blood (Foster), A., ii, 539.
    estimation of, in physiological fluids (Harding and Mason), A., ii, 501.
  Chlorates, formation of, from hypochlorites (Foerster and Dolch), A., ii, 367.
    isomorphism of nitrates and (Rea), A., i, 633.
    detection of, in presence of hypochlorites (Wischo), A., ii, 539.
  Hypochlorites, conversion of, into chlorates (Foerster and Dolch), A., ii, 367.
    estimation of, volumetrically (Bury), A., ii, 216.

- **Chlorine**:—
  - **Hypochlorites**, estimation of free chlorine in (Dienert and Wandenbulcke), A., ii, 419.
  - **Perchloric acid**, additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 209.
  - **Perchlorates**, electrolytic preparation of (Bennett and Mack), A., ii, 199; (Mack), A., ii, 256.
    - recovery of, from residues (Vürtheim), A., ii, 568.
    - detection of, microchemically (Denigès), A., ii, 419.
    - detection of, in presence of other per-salts (Monnier), A., ii, 98.
- **Chlorine detection and estimation**:—
  - detection of, in water (Le Roy), A., ii, 98.
  - estimation of, gravimetrically (Murmann), A., ii, 38.
  - estimation of, in blood serum (Laudat), A., ii, 539.
  - estimation of, iodometrically, in chlorides (Torossian), A., ii, 500.
  - estimation of, in foods, volumetrically (Weitzel), A., ii, 501.
  - free, estimation of, in hypochlorites (Dienert and Wandenbulcke), A., ii, 419.
  - estimation of, in urine (Heiduschka), A., ii, 38.
- **Chlorophyll**, photochemical experiments with (Jörgensen and Kidd), A., i, 74.
- **Chloroplatinic acid.** See under Platinum.
- **Chocolate**, estimation of caffeine and theobromine in (Savini), A., ii, 109.
- **β-Choladienecarboxylic acid** (Wieland and Sorge), A., i, 685.
- **Cholestane**, *di*chloro- (Windaus), A., i, 265.
- **Cholestanediol** (Windaus), A., i, 265.
- **Cholesterol** (Windaus), A., i, 265.
  - absorption of (Mueller), A., i, 65.
  - and its esters in blood (Bloor and Knudson; Denis), A., i, 236.
  - formation of esters of, in fatty degeneration (Valentin), A., i, 715.
  - butyrate (Salkowski), A., i, 716.
  - alcohols derived from, physiological behaviour of (Windaus), A., i, 610.
  - estimation of (Luden), A., ii, 275; (Mueller), A., ii, 393.
  - estimation of, in blood (Bloor), A., ii, 235.
  - estimation of, colorimetrically, in serum (Weston), A., ii, 156.
  - separation and estimation of, by digitonin (Prescher), A., ii, 275.
  - separation of, from fats and oils (Prescher), A., ii, 514.
- **Cholic acid**, condensation of formaldehyde and (Synthetic Patents Co.), A., i, 318.
  - salts of, activation of lipase by (de Jonge), A., i, 362.
- **Choline**, estimation of (Fühner), A., ii, 109.
- **Chondrosamine**, synthesis of (Levene), A., i, 633.
- **Chromanones** (Pfeiffer and Grimmer), A., i, 661.
- **Chromic acid**. See under Chromium.
- **Chromite**, nickel and cobalt in (Piña de Rubies), A., ii, 214.
- **Chromium alloys** with iron and nickel, analysis of (Reid), A., ii, 392.
- **Chromium compounds**, magneto-chemistry of (Cabrera and Marquina), A., ii, 355.
- **Chromium** chloride, dialysis of, and preparation of the hydrated oxide (Neidle and Barab), A., ii, 262.
  - **Chromic** oxide, adsorption of, by hide powder (Davison), A., ii, 241.
  - **Chromic-chromous** electrode. See Electrode.
  - **Chromic acid**, estimation of, iodometrically, in presence of ferric iron (Barnebey), A., ii, 274.
  - **Chromates**, estimation of, in presence of dichromates (Sacher), A., ii, 337.
  - **Dichromates**, estimation of, in presence of chromates (Sacher), A., ii, 337.
- **Chromium** phosphate (Joseph and Rae), T., 196; A., ii, 210.
- **Chromium estimation**:—
  - estimation of (Travers), A., ii, 511.
  - estimation of, in extracts and infusions (Appelius and Schmidt), A., ii, 44.
  - estimation of, in ferrochrome (Herwig), A., ii, 104; (Schumacher), A., ii, 337; (Koch), A., ii, 337, 392.
  - estimation of, in steel (Kelley, Adams, and Wiley), A., ii, 512.
  - estimation of, in steel and slags (Koch), A., ii, 221.
- **Chromoisomerism** (Hantzsch), A., i, 708.
- **Chromones.** See Benzopyrones.
- **Chromophores**, function of (Lifschitz), A., ii, 62, 435.
  - state of saturation of (Kauffmann), A., i, 391; (Lifschitz), A., i, 558.
  - auxochromic (Kauffmann), A., i, 394.
- **Chrysanthemin**, and its salts (Willstätter and Bolton), A., i, 43.
- *Chrysanthemum*, anthocyanin of (Willstätter and Bolton), A., i, 43.
- *Chrysanthemum cinerariæfolium*, manganese in stem and flowers of (McDonnell and Roark), A., i, 720.

Chrysarobin (Hesse), A., i, 276.
  commercial, constituents of (Eder), A., i, 462.
*allo***Chrysoketone** (3:4-*benzofluorenone*) (Pfeiffer), A., i, 115; (Schaarschmidt), A., i, 274.
Chrysothrix nolitangere, colour of (Senft), A., i, 506.
Cider vinegar, acetylmethylcarbinol in (Balcom), A., i, 313.
Cincholeuponic acid, ethyl ester (Rabe, Pasternack, and Kindler), A., i, 284.
Cinchona alkaloids (Rabe and Pasternack), A., i, 216; (Rabe and Böttcher), A., i, 281; (Kaufmann), A., i, 471.
  degradation of (Kaufmann, Rothlin, and Brunnschweiler), A., i, 50.
Cinchonidine, rotatory power of (Biddle and Watson), A., i, 471.
  compound of mercuric nitrite and (Rây), T., 508; A., i, 470.
Cinchonine, rotatory power of (Biddle and Watson), A., i, 471.
α-*iso***Cinchonine**, constitution of (Rabe and Böttcher), A., i, 281.
Cinchoticine, derivatives of (Kaufmann and Haensler), A., i, 472.
Cinchotinone, and its derivatives, and bromo- (Kaufmann and Haensler), A., i, 472.
Cinchotoxine, rotatory power of (Biddle and Watson), A., i, 471.
Cineole, reduction of, and its action with magnesium organic compounds (van Duin), A., i, 655.
Cinnamic acid, stereoisomeric alkyl derivatives of (Stoermer, Grimm, and Laage), A., i, 647.
  compounds of, with tartaric acid (Erlenmeyer and Hilgendorff), A., i, 26.
  p-nitrobenzyl ester (Lyman and Reid), A., i, 331.
Cinnamic acid, *o*-, *m*-, and *p*-nitro-, *p*-nitrobenzyl esters (Lyons and Reid), A., i, 559.
Cinnamylideneazobenzene-*p*-hydrazone salts (Tröger and Piotrowski), A., i, 668.
Cinnamylidene-*p*-chlorobenzeneazo-α-naphthylhydrazone (Tröger and Piotrowski), A., i, 669.
Cinnamylidenemalonylthiocarbamide (Dox and Plaisance), A., i, 53.
Cinnamylidenemethyl methyl ketone, action of furfuraldehyde on (Giua), A., i, 408.
Citarine, use of, in preparation of colloidal metals (Vanino), A., ii, 299.
Citric acid, formation of, by fermentation of sugar by *Aspergillus niger* (Currie), A., i, 614.
  azides and hydrazides of, and their derivatives (Curtius and Sauvin), A., i, 639.
  p-nitrobenzyl ester (Reid), A., i, 334.
  detection of (Broeksmit), A., ii, 429.
  estimation of (Willaman), A., ii, 51.
  estimation of, and the physiological action of its sodium salt (Salant and Wise), A., i, 106.
Citronellaldehyde, action of acids on (Prins), A., i, 513.
Citronellaldehydes, isomeric (Prins), A., i, 538.
Clay, refractory properties of (Le Chatelier and Bogitch), A., ii, 319.
Clover, sweet, *l*-leucine in silage from (Plaisance), A., i, 721.
  estimation of starch in (v. Fellenberg), A., ii, 515.
Coagulation (Zsigmondy), A., ii, 366.
  action of salts on (Schryver and Hewlett), A., ii, 22.
Coagulating capacity, relation of, to constitution (Gann), A., ii, 21.
Coal, bituminous, composition of different forms of (Mabery), A., ii, 537.
  solvents of (Wahl), A., ii, 324.
  distillation of, under pressure (Capps and Hulett), A., i, 689.
  oxidation of (Charpy and Godchot), A., ii, 103.
  analysis of (Gröppel), A., ii, 384.
Coal gas, liquid purification of (Espenhahn), A., ii, 310.
  burning, action of, on platinum (Mylius and Hüttner), A., ii, 482.
  action of, on plants (Wehmer), A., i, 531, 618; (Doubt), A., i, 619.
  estimation of naphthalene in (Knublauch), A., ii, 427.
Coal mines, formation of hydrogen sulphide by gob fires in (Drakeley), T., 853; A., ii, 530.
Coal tar, optical activity of (Fischer and Gluud), A., i, 258.
  thermal decomposition of (Jones), A., i, 193.
Coal-tar colouring matters, physiology of (Salant and Bengis), A., i, 70.
Coal-tar oil, estimation of benzene and toluene in (Harker), A., ii, 338.
Cobaltammines. See Cobalt bases.
Cobalt, ionic mobility of (Lorenz and Posen), A., ii, 14, 15, 439.
Cobalt aluminate, stannate and zincate, formation of (Hedvall), A., ii, 35.
  azide (Wöhler and Martin), A., i, 383.

Cobalt chloride, absorption of light by solutions of, in water and alcohols (Hulbert, Hutchinson, and Jones), A., ii, 161.
  Cobalto-cobaltic oxide, dissociation temperature of (Hedvall), A., ii, 15.
Cobalt, estimation of (Powell), A., ii, 220.
  estimation of, in ores and alloys (Schoeller and Powell), A., ii, 425.
  estimation and separation of (Carnot), A., ii, 391.
Cobalt bases (*cobaltammines*) (Harkins, Hall, and Roberts), A., ii, 94.
  absorption spectra of (Shibata and Matsuno), A., ii, 186.
  isomeric, relation between the physical properties and electro-valencies of (De), T., 51 ; A., ii, 165.
Cobalt hygrometers, history and preparation of (Vanino), A., ii, 320.
Cobra poison. See Poison.
Cocaine, compound of mercuric nitrite and (Rây), T., 509 ; A., i, 470.
Codeine, compound of mercuric nitrite and (Rây), T., 508 ; A., i, 470.
Codeine, hydroxy-, and its derivatives (Freund and Speyer), A., i, 218.
Codeinone, hydroxy-, and its derivatives (Freund and Speyer), A., i, 217.
Collargol, preparation of (Gerasimov), A., i, 98.
Collidinium, palladi- and pallado-chlorides (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.
  palladotribromide (Gutbier and Fellner), A., i, 542.
Colloids, chemistry of (Hekma), A., ii, 22, 23.
  structure of (Fischer and Hooker), A., ii, 132.
  preparation of (Ghosh), A., ii, 563.
  action of radium rays on (Fernau and Pauli), A., ii, 189.
  physical changes in (Pauli and Matula), A., i, 419.
  osmotic pressure of (Biltz, Bugge, and Mehler), A., ii, 17.
  compressibility of (Westgren), A., ii, 452.
  protective (Gutbier and Weise), A., ii, 21, 131 ; (Gutbier and Wagner), A., ii, 131, 168, 169 ; (Gutbier and Kräutle), A., ii, 244, 298, 299.
  agglutination of, by non-electrolytes (Freundlich and Rona), A., ii, 365.
  powdered, action of salts on swelling of, and of animal membranes (Loeb), A., ii, 453.
Colloidal solutions, refraction of (Wiegner), A., ii, 185.
  specific volume of (Kruyt), A., ii, 407.
  viscosity and hydration of (Arrhenius), A., ii, 130.
  effect of dispersion of particles on the colour of (Harrison), A., ii, 131.
  coagulation of (v. Smoluchowski), A., ii, 297.
  precipitation of (Kruyt and van der Spek), A., ii, 563.
Colophony, ammonium soaps of (Paul), A., i, 214.
Colorimeter, new (Moreau), A., ii, 418.
Colorimeter-nephelometer (Kober), A., ii, 266.
Colorimetry, errors in (Dehn), A., ii, 499.
Colour and chemical constitution (Kauffmann), A., i, 391, 394 ; (Kehrmann and Hempel), A., i, 593 ; (Moir), A., ii, 349, 557.
  of salts of compounds resembling alloxantin, theory of (Retinger), A., i, 519.
  method of defining and estimating (Ostwald), A., ii, 281.
Colour lakes, theory of (Baudisch), A., i, 556.
Colouring matter, $C_{20}H_{18}O_2N_2$ (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 225.
Colouring matters, absorption spectra of (Ghosh and Watson), T., 815 ; A., ii, 523.
  action of water on (Dehn), A., i, 578.
  lichens used as (Ryan and O'Riordan), A., i, 342.
  oxidation of, in living cells (Schläpfer), A., i, 187.
  staining of cells by (Schulemann), A., i, 369, 429, 612 ; (Skraup), A., i, 369.
  organic, spectra of (Pokorný), A., ii, 402.
    absorption of, by soils (zu Leiningen), A., ii, 112.
  vat (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 225.
  See also :—
    Bilirubin.
    Helicorubin.
    Serratulin.
Combustion (Richards and Davis), A., ii, 237.
  of organic compounds and chemical affinity (Thornton), A., ii, 357.
  in an enclosed volume of air (Müller), A., ii, 463.

Combustion, effect of partial pressure of oxygen on (DOLLWIG, KOLLS, and LOEVENHART), A., ii, 569.
Conarachin (JOHNS and JONES), A., i, 191.
Concanavalin (JONES and JOHNS), A., i, 191.
Condenser, new (FISHBURN), A., ii, 305.
  universal reflux (VIGREUX), A., ii, 198.
Conductivity water. See under Water.
Coniine, compound of mercuric nitrite and (RÂY), T., 507; A., i, 470.
Copper, occurrence of, in the Komandor Islands, Bering Sea (MOROZEWICZ), A., ii, 483.
  occurrence of, in plants of a copper-tailing district (BATEMAN and WELLS), A., i, 373.
Copper alloys with glucinum (OESTERHELD), A., ii, 89.
  with iron (RUER and GOERENS), A., ii, 474.
  with iron, nickel, and tungsten (IRMANN), A., ii, 478.
Copper haloids, compounds of, with haloids of substituted ammonium bases (DATTA and SEN), A., i, 323.
  sulphate, action of, on algæ in drinking-water (BADO), A., i, 107.
  sulphide, secondary enrichment of deposits of (ZIES, ALLEN, and MERWIN), A., ii, 91.
    properties of colloidal solutions of (YOUNG and NEAL), A., ii, 167.
  Cupric chloride, solubility of, in pyridine (MATTHEWS and SPERO), A., i, 518.
    iodide, decomposition and re-formation of (ELBS), A., ii, 371.
    cuprous sodium thiosulphate ammoniate (BENRATH), A., ii, 260.
  Cuprous fulminate (WÖHLER and MARTIN), A., i, 383.
    oxide, precipitated, estimation of (ROLLE), A., ii, 104.
    sulphide, equilibrium of antimony sulphide and (CHIKASHIGE and YAMAUCHI), A., ii, 143.
Copper organic compounds:—
  ferrocyanide, properties of membranes of (TINKER), A., ii, 363.
Copper detection, estimation, and separation:—
  detection of, with hydrogen peroxide (MAYER and SCHRAMM), A., ii, 334.
  estimation of (HAHN), A., ii, 543.
  estimation of, in alloys (HAGMAIER), A., ii, 181.
  estimation of antimony, lead, and (HOWDEN), A., ii, 580.
  separation of nickel and (GROSSMANN and MANNHEIM), A., ii, 512.
Corchorus capsularis (jute), seeds of. See Seeds.
Corks, treatment of, to render them air-tight (WARD), A., ii, 538.
Corn gluten, value of proteins as supplements for (OSBORNE, MENDEL, FERRY, and WAKEMAN), A., i, 237.
Corydaline, stereoisomeric forms of, and their derivatives (GADAMER and KLEE), A., i, 472.
Corydalis alkaloids (GADAMER and KLEE), A., i, 472.
Cotoporphyrin, constitution of, and *tetra*chloro-, dihydrochloride (FISCHER), A., i, 712.
Cotton fibres, chemical and physical properties of (HALLER), A., i, 436.
Cotton-seed meal, inositol-phosphoric acids of (RATHER), A., i, 315.
  nutrition experiments with (RICHARDSON and GREEN), A., i, 524, 604.
  toxicity of (CARRUTH), A., i, 719.
Cotton-seed oil, partition of alcohols between water and (WROTH and REID), A., ii, 17.
  hydrogenation of (MOORE, RICHTER, and VAN ARSDEL), A., i, 442.
o-**Coumaramide** (WEERMAN), A., i, 560.
p-**Coumaramide** (FISCHER and NOURI), A., i, 393.
Coumaric acid, *p*-nitrobenzyl ester (LYONS and REID), A., i, 559.
  propyl ester (v. AUWERS), A., i, 267.
Coumarin, iodine additive product of (DOX and GAESSLER), A., i, 346.
  periodides (SIMONIS), A., i, 705.
Coumarin-8(or 6)-carboxylic acid, 4:5:7-*tri*hydroxy-, ethyl ester, benzylidene derivatives of (SONN), A., i, 277.
p-**Coumaronitrile** (FISCHER and NOURI), A., i, 393.
Covellite, dissociation pressure of (ALLEN and LOMBARD), A., ii, 194.
Crandallite (LOUGHLIN and SCHALLER), A., ii, 146.
Creatine, origin of (BAUMANN and HINES), A., i, 677.
  influence of arginine on, in rabbits' muscle (THOMPSON), A., i, 369.
  change of arginine into, in the animal body (JANSEN), A., i, 606.
  excretion of (LYMAN and TRIMBY), A., i, 240.
  excretion of, in children (DENIS, KRAMER, and MINOT), A., i, 526.
  excretion of, in man (DENIS and MINOT), A., i, 496.
  excretion of, in urine (DENIS and MINOT), A., i, 367, 676.
  estimation of, in blood (WILSON and PLASS), A., i, 360; (GREENWALD), A., i, 523.

Creatinine, excretion of (Lyman and Trimby), A., i, 240.
  estimation of (Hunter and Campbell), A., ii, 110; (Folin and Doisy), A., ii, 159.
  estimation of, colorimetrically (Gerret), A., ii, 225.
  estimation of, in blood (Wilson and Plass), A., i, 360; (Gettler and Oppenheimer), A., ii, 184.
Creosole, bromo- (Krauss and Crede), A., i, 557.
Creosote from maplewood, constituents of (Pieper, Acree, and Humphrey), A., i, 452.
Creosotic acids, *p*-nitrobenzyl esters (Lyons and Reid), A., i, 559.
p-**Cresol** 3-*di*sulphide, 2:4-*di*bromo-, and its acetyl derivative (Zincke and Arnold), A., i, 264.
o-**Cresol**, 6-bromo-4-amino-, acetyl derivative, hydrobromide (Jacobs and Heidelberger), A., i, 697.
p-**Cresol**, 5-iodo-3-nitro-, and its ammonium salt (Datta and Prasad), A., i, 332.
  3-thiol-, and its derivatives (Zincke and Arnold), A., i, 263.
Cresols, electrolytic oxidation of (Pomilio), A., i, 332.
  compounds of, with pyridine (Hatcher and Skirrow), A., i, 665.
p-**Cresol-3-sulphinic acid** (Zincke and Arnold), A., i, 264.
o-**Cresolsulphonephthalein**, *di*bromo-, as an indicator for use with milk cultures (Clark and Lubs), A., ii, 499.
Cristobalite (Le Chatelier), A., ii, 97.
Critical point, second, existence of (Prud'homme), A., ii, 192.
  temperature, ratio of the boiling point to (Herz), A., ii, 14.
Crocetin, detection of (Tunmann), A., ii, 58.
Crotonic acid, amino-, ethyl ester, acyl derivatives of (Benary, Reiter, and Soenderop), A., i, 252.
  αβ-thio-, and its salts (Rây and Dey), T., 510; A., i, 441.
α-**Crotonic acid** in soils (Walters and Wise), A., i, 376.
Crustaceans, deposits of lime salts in (Paul and Sharpe), A., i, 66.
Cryogenine, detection of, in urine (Grimbert), A., ii, 344; (Justin-Mueller), A., ii, 518.
Cryoscopy, apparatus for (Mathews), A., ii, 356.
  with fenchone as solvent (Jona), A., ii, 524.
Cryostat for the range 27–35° (Onnes), A., ii, 407.
Cryptopine (Perkin), A., i, 280.
Crystals, structure of (Pfeiffer), A., ii, 78; (Fock; Niggli), A., ii, 129; (v. Laue; Rinne), A., ii, 166; (Schoenflies), A., ii, 447.
    and chemical constitution (Groth), A., ii, 446.
    and valency (Beckenkamp), A., ii, 296.
  change in structure of, due to replacement of elements (W. and D. Asch), A., ii, 449.
  Röntgen ray spectra of (Smits and Scheffer), A., ii, 78.
  action of Röntgen rays on (Olie and Byl), A., ii, 286.
  interference effects of, in Röntgen rays (Debye and Scherrer), A., ii, 437.
  relation between density and refractive index of (Rosický), A., ii, 433.
  atomic volume and valency in (Tutton), A., ii, 244.
  stereochemistry of (Rinne), A., ii, 18.
  growth of, in fusions (Nacken), A., ii, 363.
  growth and symmetry of (Schubnikov), A., ii, 450.
  pressure exerted by, during growth (Long), A., ii, 243.
  influence of temperature variation on formation of (Schubnikov), A., ii, 449.
  orientation of anisotropic liquids on (Grandjean), A., ii, 451.
  drainage of (Hall), A., ii, 363.
  liquid, production of (Gaubert), A., ii, 113.
    rotatory power of (Gaubert), A., ii, 188.
  mixed (Kruyt and Heldermann), A., ii, 81; (Viola), A., ii, 297.
    constitution of (Vegard and Schjelderup), A., ii, 243.
    resistance limits of (Tammann), A., ii, 448.
  analysis of (Vegard), A., ii, 296.
Crystallisation in four-component systems (Boeke), A., ii, 195.
  velocity of. See Velocity.
Crystallography and Röntgen rays (v. Laue), A., ii, 166.
Crucible, Gooch, improved (Korten), A., ii, 326.
Culture solutions for the bacteriological analysis of water (Chamot and Sherwood), A., ii, 556.
ψ-**Cumene**, effect of, on the olfactory organ (Backman), A., i, 498.
ψ-**Cumidine** aminosulphonate (Paal and Hubaleck), A., i, 643.

ψ-Cumidinium palladochloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.

ψ-Cumylaminosulphonic acid, and its salts (Paal and Hubaleck), A., i, 643.

ψ-Cumylnitrosoaminosulphonic acid (Paal and Hubaleck), A., i, 644.

ψ-Cumylsulphamic acid. See ψ-Cumylaminosulphonic acid.

β-*iso*Curcumin (Heller), A., i, 705.

Cyanamide, preparation of, from its calcium derivative (Werner), A., i, 82.

constitution of (Colson), T., 554; A., i, 448.

preparation of carbamide from (Schmidt), A., i, 688.

formation of guanidine from (Schmidt), A., i, 449.

Cyanamides, action of Grignard reagents on (Adams and Beebe), A., i, 96.

Cyanogen:—

Hydrocyanic acid, occurrence and estimation of, in *Sorghum vulgare* (Willaman), A., i, 245, 246.

potassium salt, rate of hydrolysis of (v. Zawidzki and Mieczyński), A., ii, 81.

detection of (Anderson), A., ii, 182.

Cyanides, detection of, biochemically (Jacoby), A., ii, 54.

Cyanic acid, use of, in glacial acetic acid (Bailey and Moore), A., i, 355, 587.

Cyanotrichite from Traversella (Colomba), A., ii, 377.

Cyanuric acid in soils (Wise and Walters), A., i, 622.

p-nitrobenzyl ester (Lyons and Reid), A., i, 559.

n- and *iso*-**Cyanuric acids,** salts and esters of, and their isomerism and molecular complexity (Billmann and Bjerrum), A., i, 382.

Cydonia seeds. See Seeds.

Cypridina hilgendorfii, bioluminescence in (Harvey), A., i, 365.

Cystine, diethyl ester hydrochloride of (Abderhalden and Wybert), A., i, 121.

Cytosine-uracil-dinucleotide, barium and brucine salts of (Levene), A., i, 670.

D.

Dahllite from Greenland (Bøggild), A., ii, 145.

Deamidisation in plants (Schweitzer), A., i, 504.

Dehydrocamphor. See β-*pericyclo*Camphanone.

Dehydrothebaine, and its methiodide (Freund and Speyer), A., i, 219.

Density, determination of, of gases (Edwards), A., ii, 442.

of gases and liquids, formula for calculation of (Schmidt), A., ii, 406.

relation between refractive index and (Rosický), A., ii, 433.

Deoxybenzoin, 2:4-*di*nitro-, and its derivatives (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 207.

Deoxycantharidic acid, and its silver salt (Rudolph), A., i, 469.

Deoxycantharidin (Rudolph), A., i, 469.

Deoxycholic acid, preparation of (Mair), A., i, 442.

distillation of (Wieland and Sorge), A., i, 685.

Deoxylithofellic acid (Fischer), A., i, 4.

Desiccating agents, efficiency of (McPherson; Dover and Marden), A., ii, 500.

Desiccator, efficient (Pratt), A., ii, 255.

vacuum electrically heated (Robertson and Schmidt), A., ii, 28.

"**Detonal.**" See α-Ethylbutyrylmethane.

Dextrin, adsorption of (Rakuzin), A., ii, 294.

Dextrose, rotatory power of (Foulkes), A., i, 79.

mutarotation of (Hudson and Dale), A., i, 320.

turbidity of solutions of, and of their mixtures with maltose (Homberger and Marvel), A., i, 370.

action of alkalis on (Waterman), A., i, 195, 631.

concentration of, in animal tissues (Palmer), A., i, 494.

concentration of, in blood (Hiller and Mosenthal), A., i, 99.

effect of the pancreas on, in blood (v. Körösy), A., i, 714.

metabolism of. See Metabolism.

fermentation of, by yeast (Wilenko; v. Euler and Haldin), A., i, 680.

tetra-acetyl derivative, compounds of, with 2-phenylquinoline-4-carboxylic acid and with salicylic acid (Karrer), A., i, 540.

estimation of, in blood (Schumm), A., i, 713; (Bauzil and Boyer; McGuigan and Ross), A., ii, 548.

estimation of, in muscle (Hoagland), A., ii, 515.

estimation of, in urine (Frerichs and Mannheim), A., ii, 393; (Hiller), A., ii, 394; (Burmann), A., ii, 514.

Dextrose, detection and estimation of arsenic in (Kling), A., ii, 579.
  estimation of arsenic in (Muttelet), A., ii, 101.

Diabetes (McDanell and Underhill), A., i, 368; (Macleod and Hoover), A., i, 426.
  theory of (Sansum and Woodyatt), A., i, 496.
  experimental (Macleod, Fulk, Davis, and Scott), A., i, 367.
  acidosis in (Stillman, van Slyke, Cullen, and Fitz), A., i, 523.
  diastatic activity of blood in (Myers and Killian), A., i, 369.
  formation of acetoacetic acid and lactic acid in the liver in (Embden and Isaac), A., i, 496.
  metabolism in (v. Euler and Svanberg), A., i, 68.
  influence of sodium carbonate in (Murlin, Craver, Niles, and Coleman), A., i, 104.
  pancreatic, in the dog (Murlin and Kramer; Kramer, Marker, and Murlin; Murlin, Kramer, and Riche), A., i, 69; (Murlin and Sweet), A., i, 104.

Diacetanilide, *p*-nitro-, crystallography of halogen derivatives of (Artini), A., i, 553.

2:6-Diacetatomercuriphenol-*p*-sulphonic acid, sodium salt (Rupp and Herrmann), A., i, 488.

2:6-Diacetatomercurithymol (Rupp), A., i, 670.

3:4-Diacetoxybenzonitrile. See Protocatechuonitrile diacetate.

$\beta\gamma$-Diacetoxypentamethylene-oxide (Borsche), A., i, 118.

2:4-Diacetyl-3:5-dimethoxytoluene, and its derivatives (Algar), A., i, 345.

Diacetylglyceraldehyde dimethylacetal (Wohl and Momber), A., i, 319.

Diacetylmalonic acid, ethyl ester, constitution of (v. Auwers and Auffenberg), A., i, 627.

Diacetylorcinol, derivatives of (Algar), A., i, 345.

Diacetyltartaric acid, *iso*butyl ester, rotation of (Patterson), A., ii, 3.

Dialanyl-*l*-cystines (Abderhalden and Wybert), A., i, 120.

Dialkyl hydrogen phosphates, preparation and ionisation of (Drushel and Felty), A., i, 126.

Diallylacetonedicarboxylic acid, ethyl ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 146.

1:3-Diallyl*cyclo*butane-2:4-dione-1-carboxylic acid, ethyl ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 147.

Dialysis (Neidle and Barab), A., ii, 262.
  preparation of membranes for (Brown), A., ii, 362.
  apparatus for (Thoms), A., ii, 561.

Diamonds, formation of (Ruff), A., ii, 369.

Di*iso*amylammonium palladi- and pallado-chlorides (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.

Di*iso*amylparabanic acid (Stieger), A., i, 172.

Di*iso*amylthioparabanic acid (Stieger), A., i, 172.

4:4′-Dianilinodiphenyl, 3:5:3′:5′-*tetra*nitro- (Borsche and Scholten), A., i, 391.

Di-*p*-anisylbenzylcarbinol (Coma y Roca), A., i, 266.

Dianisylideneaminodiphenyl-*p*-azophenylene, *di*amino- (Heiduschka and Goldstein), A., i, 484.

Dianthraquinonylene dioxides, preparation of (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 41.

Diarylsulphones (Hinsberg), A., i, 135.

Diastase, optical properties and adsorption of (Rakuzin and Flier), A., i, 181.
  theory of action of (Woker), A., i, 61.
  formaldehyde as a substitute for (v. Kaufmann), A., i, 251; (Woker), A., i, 447.
  effect of soaps on the action of (Kende), A., i, 615.
  digestion of starch with (Pauletig), A., i, 670.
  animal (Myers and Killian), A., i, 369.
  of malt, influence of hydrion activity on activity of (Adler), A., i, 61.

Diazoacetic acid, ethyl ester, action of heat on derivatives of (Staudinger and Hirzel), A., i, 178.

Diazo-compounds (Staudinger and Hirzel), A., i, 178.
  action of copper acetylide on (Scharvin and Plachuta), A., i, 179.

***p*-Diazoiminobenzene**, acyl derivatives of (Morgan and Upton), T., 187; A., i, 300.

Diazomethane, preparation of (Loring), A., i, 515.

Diazo-oxides, internal (*diazophenols*), constitution of (Morgan and Tomlins), T., 497; A., i, 481.

Diazo-reaction, method of carrying out the (Zucker and Ruge), A., ii, 112.

6:6′-Dibenzeneazo-3:3′-diphenol, and its dimethyl ether (Borsche), A., i, 558.

αγ-**Dibenzoyl-*β*-3-bromo-4-methoxyphenylbutyric acid**, methyl ester (Kohler and Conant), A., i, 570.

1:2-Dibenzoyl-3-*m*-bromo-*p*-methoxyphenyl*cyclo*propane-1-carboxylic acid, and its methyl ester (Kohler and Conant), A., i, 570.

αδ-**Dibenzoylbutadiene**, *αδ*-*di*cyano- (Kauffmann and Jeutter), A., i, 395.

Dibenzoylpentamethylenediamine-*pp*′-diarsine oxide (Sieburg), A., i, 487.

Dibenzoyl*iso*propylidenebenzidine (Turner), T., 4; A., i, 130.

Dibenzyl. See *s*-Diphenylethane.

Dibenzyl sulphide. See Benzyl sulphide.

Dibenzylamine, 2:6-*di*- and 2:6:2′:6′-*tetra*-nitro-, and their salts (Reich and Oganessian), A., i, 554.

Dibenzylbenzamidine, and its hydrochloride (Adams and Beebe), A., i, 97.

Dibenzylideneaminodiphenyl-*p*-azophenylene, *di*amino-, *di*-*p*-nitro-derivative (Heiduschka and Goldstein), A., i, 484.

Dibenzylpropenylamidine hydrochloride (Adams and Beebe), A., i, 96.

Dibenzylsulphone-dimethylethylenediamine, -ethylenediamine, and **-methylethylenediamine** (Johnson and Bailey), A., i, 10.

Dibenzyl-*p*-tolenylamidine, salts of (Adam and Beebe), A., i, 97.

"**Dibnal.**" See *α*-Butylhexoylurethane.

Di*iso*butylammonium palladi- and pallado-chlorides (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541; (Gutbier and Fellner), A., i, 542.

Di-*tert.*-butyloxamide (Brander), A., i, 555.

αγ-**Dicamphorylidenepropane** (Rupe and Burckhardt), A., i, 142.

Dicoumarinyl, 3:3′-thio- (Stieger), A., i, 173.

Dicyanodiamide, estimation of, in nitrolime (Stutzer), A., ii, 159; (Hager and Kern), A., ii, 518.

Dicinnamylideneacetone, additive compound of perchloric acid and (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 209.

Didehydrocorydalinesulphonic acid (Gadamer and Klee), A., i, 473.

Di-*αα*-diphenylethyloxamide (Brander), A., i, 555.

Diet, effect of, on growth (Robertson), A., i, 65; (Osborne and Mendel), A., i, 238.
  removal and replacement of amino-acids in (Ackroyd and Hopkins), A., i, 237; (Geiling), A., i, 605.
  importance of vitamines in (Osborne, Mendel, Ferry, and Wakeman), A., i, 603; (McCollum and Pitz), A., i, 604.
  leaf and seed mixtures as, compared with mixtures of seed and seed (McCollum, Simmonds, and Pitz), A., i, 49.
  of oats, effect of, on urea in blood and tissues (Lewis and Karr), A., i, 100.
  potatoes as source of protein in (Rose and Cooper), A., i, 524.

4:5-Diethoxy-1:3-dimethyl-4:5-dihydrouric acid (Biltz and Strufe), A., i, 296.

4:5-Diethoxy-1:7-dimethyl-4:5-dihydrouric acid (Biltz and Damm), A., i, 295.

2:6-Diethoxy-3:5-dimethyl-1:4-pyrone (Schroeter, Kesseler, Liesche, and Müller), A., i, 147.

Diethoxydinaphthyl ketone (Giua), A., i, 204.

4:5-Diethoxy-1-methyl-4:5-dihydrouric acid (Biltz and Strufe), A., i, 293.

2:3-Diethoxyphenanthraphenazine (G. M. and R. Robinson), T., 934.

Diethoxyphenyltartramide (Casale), A., i, 643.

4:5-Diethoxy-1:3:7-trimethyl-9-ethyl-4:5-dihydrouric acid (Biltz and Bergius), A., i, 589.

4:5-Diethoxy-3:7:9-trimethyl-1-ethyl-4:5-dihydrouric acid (Biltz and Max), A., i, 590.

Diethylacetonedicarboxylic acid, ethyl ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 146.

Diethylamine, physical constants of (Berthoud), A., ii, 237.

p-**Diethylamino-*o*-benzhydryltriphenylcarbinol** (Pérard), A., i, 652.

p-**Diethylaminobenzyltriphenylcarbinol** (Pérard), A., i, 653.

Diethylaminocodide, and its platinichloride (v. Braun and Kindler), A., i, 164.

1-*p*-Diethylamino-2:2-diphenyl-1:2-dihydro*iso*benzofuran, 1-hydroxy-, and its derivatives (Pérard), A., i, 652.

Diethylamino-*m*-hydroxybenzoyl*tetra*chlorobenzoic acid, preparation and derivatives of (Orndorff and Rose), A., i, 30.

β-Diethylamino-β′-phenoxy*iso*propyl alcohol, and its hydrochloride and benzoate (Pyman), T., 170; A., i, 304.
5-Diethylamino-ψ-uric acid (Biltz and Heyn), A., i, 288.
6-Diethylaminoxanthone-1-carboxylic acid, 2:3:4-*tri*chloro-, and its salts and derivatives (Orndorff and Rose), A., i, 31.
Diethylammonium palladichloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 542.
o-**Diethylbenzene,** *di*-β-amino-, and its derivatives (v. Braun, Kruber, and Danziger), A., i, 131.
1:3-Diethyl*cyclo*butane-2:4-dione, and its derivatives (Schroeter, Kesseler, Liesche, and Müller), A., i, 149.
1:3-Diethyl*cyclo*butane-2:4-dionecarboxylic acid, esters of (Schroeter, Kesseler, Liesche, and Müller), A., i, 147.
Diethyl*cyclo*butanedionedicarboxylic acid, ethyl ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 148.
2:2-Diethylhydrindene (Freund, Fleischer, and Gofferjé), A., i, 574.
Diethyl*cyclo*pentamethyleneplumbine (Grüttner and Krause), A., i, 123.
Diethylthiazine, and its salts (Kehrmann, Robert, and Sandoz), A., i, 226.
Diethyl*di*thiocarbamylsuccinamic acids (Kallenberg), A., i, 280.
Diethylthiocarbamylsuccinic acids (Kallenberg), A., i, 280.
Diffusion (Hamburger), A., ii, 562.
  and adsorption (Alexander), A., ii, 242.
    rhythmic (Stansfield), A., ii, 125.
      in gelatin-salt jellies (Moeller), A., ii, 410.
  of gases, apparatus for (Marcus), A., ii, 409.
  in liquids (Clack), A., ii, 75.
Diffusion coefficient, calculation of (Griffiths), A., ii, 294.
Difurfurylidenetricinnamylideneacetone (Giua), A., i, 408.
3:5′-Difuryldihydro-1:2-triazolotriazole, 5:3′-*di*hydroxy- and -*di*thiol- (Bailey and McPherson), A., i, 588.
Digestion, tryptic, of proteins (Long and Hull), A., i, 485.
Digitalis, development of glucosides in leaves of (Straub), A., i, 615.
  detection of the glucoside in leaves of (Wratschko), A., ii, 182.
Digitalis, glucosides of (Kiliani), A., i, 468.
Diglycyldi-*l*-leucyl-*l*-cystine (Abderhalden and Wybert), A., i, 120.
"**Diglycylhippenylcarbamide**" (Curtius and Petridis), A., i, 201.
Di*iso*hexoyldi-*d*-alanyl-*l*-cystine, *di*-*d*-α-bromo- (Abderhalden and Wybert), A., i, 120.
Di*iso*hexoyldiglycyl-*l*-cystine, *di*-*d*-α-bromo- (Abderhalden and Wybert), A., i, 120.
Dihippurylaminomethylcarbamide. See "Diglycylhippenylcarbamide."
N-**Dihydro-1:2:1′:2′-anthraquinoneazine.** See Indanthrene.
Dihydro-α-benzopyrones, preparation of (Fischer and Nouri), A., i, 469.
Dihydroberberine, cyano- (G. M. and R. Robinson), T., 966.
Dihydrocantharic acids (Gadamer), A., i, 660.
Dihydrochelerythrin (Karrer), A., i, 349.
Dihydrocinchonicine, hydroxy-, and its picrate (Rabe and Böttcher), A., i, 282.
Dihydrocinchoninone, hydroxy-, and its picrate (Rabe and Böttcher), A., i, 282.
Dihydrocinchotoxine. See Cinchoticine.
Dihydrocodeinone, hydroxy-, and its derivatives (Freund and Speyer), A., i, 218.
"**Dihydrocodeone,**" hydroxy-, and its oxime (Freund and Speyer), A., i, 218.
Dihydroindole derivatives, reduction of (v. Braun, Heider, and Neumann), A., i, 167.
"**Dihydro*iso*indolylpyrrolidinium**" bromide (v. Braun), A., i, 170.
"**Dihydro*iso*indolyltetrahydro*iso*quinolinium**" bromide (v. Braun), A., i, 170.
Dihydromorphine dimethyl ether hydrochloride (Mannich), A., i, 474.
2:3-Dihydro-α-naphtha-γ-pyrone, and its derivatives (Pfeiffer and Grimmer), A., i, 662.
Dihydrothebainone, hydroxy-, and its derivatives (Freund and Speyer), A., i, 218.
4:5-Dihydrouric acid, 5-amino-4-hydroxy- (Biltz and Heyn), A., i, 288.
Di-3-indolyl-*o*-aminophenylmethane, and its hydrochloride (Hoschek), A., i, 167.
2:5-Diketo-4-benzoyl-1:3-dimethyl-2:5-dihydropyrrole (Knust and Mumm), A., i, 415.
1:3-Diketo-*o*-benzoylene-2:2-dimethylhydrindenes (Freund, Fleischer, and Stemmer), A., i, 575.

(*α*)- and (*β*)-**1:3-Diketo-*α*-benzylene-2:2-dimethylhydrindenes** (Freund, Fleischer, and Stemmer), A., i, 575.

2:3-Diketodihydrothionaphthens, preparation of (Stollé), A., i, 91.

5:3′-Diketo-4:4′-diphenyl-3:5′-difurylhexahydro-1:2-triazolotriazole (Bailey and McPherson), A., i, 588.

5:3′-Diketo-4:4′-diphenyl-3:5′-distyrylhexahydro-1:2-triazolotriazole (Bailey and McPherson), A., i, 588.

5:3′-Diketo-4:4′-diphenyl-3:5′-*di-m*-nitrophenylhexahydro-1:2-triazolotriazole (Bailey and McPherson), A. i, 588.

1:3-Diketo-2:2:5:5:8:8-hexaethyltritrimethylenebenzene (Freund, Fleischer, and Gofferjé), A., i, 574.

γδ-Diketohexoic acid, α-hydroxy-, disemicarbazone of (Borsche), A., i, 118.

Diketohydrindene (*indandione*), and its aniline derivatives (Wislicenus and Pfannenstiehl), A., i, 273.

Diketohydrindenes, synthesis of (Freund, Fleischer, Gofferjé, and Stemmer), A., i, 572.

2:4-Diketo-5-ψ-indoxylidenethiazolidine (Andreasch), A., i, 664.

2:6-Diketo-5-methyl-4-*α*-ethoxyethyl pyrimidine (Johnson and Hadley), A., i, 667.

2:6-Diketo-5-methyl-4-*α*-methoxyethyl pyrimidine (Johnson and Hadley), A., i, 667.

γ-**Diketones**, action of, with unsaturated ketones (Scholtz), A., i, 462.

4:6-Diketo-1:2:2:3:5-pentaphenylpiperidine-3:5-dicarboxylic acid, methyl ester (Staudinger and Hirzel), A., i, 651.

2:4-Diketo-3-phenyl-5-*p*-aminobenzylidenethiazoline, and its derivatives (Andreasch), A., i, 663.

2:6-Diketo-4-phenyl-1-methyl-1:2:3:6-tetrahydropyridine. See *β*-Phenylglutaconmethylimide.

4:9-Diketotetrahydro-1:3:6:8-naphthatetrazine, 2:7-*di*cyanoamino- (Dox), A., i, 481.

5:3′-Diketo-3:4:4′:5′-tetraphenylhexahydro-1:2-triazolotriazole (Bailey and McPherson), A., i, 587.

Dilatometer (Escard), A., ii, 524.

Di-*l*-leucyldi-*d*-alanyl-*l*-cystine (Abderhalden and Wybert), A., i, 120.

3:4-Dimethoxyacetophenone, 2:6-*di*hydroxy- (Nierenstein), T., 7; A., i, 150.

3:4-Dimethoxybenzoic acid, 5-nitro-, and 6-nitro-2-amino-, and their derivatives (Gibson, Simonsen, and Rau), T., 74; A., i, 203.

7:4′-Dimethoxy-3-benzyl-2:3-dihydro-*γ*-benzopyrone (Pfeiffer and Grimmer), A., i, 662.

2:2′-Dimethoxy-5:5′-diacetyldiphenylmethane, 4:4′-*di*hydroxy-, and its derivatives (Pfeiffer and Grimmer), A., i, 662.

pp′-**Dimethoxydicinnamylideneacetone**, and its compound with perchloric acid (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 209.

4:5-Dimethoxy-4:5-dihydrouric acid (Biltz and Heyn), A., i, 286.

4:5-Dimethoxy-3:7-dimethyl-1:9-diethyl-4:5-dihydrouric acid (Biltz and Max), A., i, 590.

4:5-Dimethoxy-1:3-dimethyl-4:5-dihydrouric acid (Biltz and Strufe), A., i, 296.

4:5-Dimethoxy-1:7-dimethyl-4:5-dihydrouric acid (Biltz and Damm), A., i, 295.

4:4′-Dimethoxy-2:2′-dimethyl-1:1′-dithioxanthonyl (Ullmann and v. Glenck), A., i, 161.

4:5-Dimethoxy-3:7-dimethyl-1-ethyl-4:5-dihydrouric acid (Biltz and Max), A., i, 591.

2:6-Dimethoxy-3:5-dimethyl-1:4-pyrone (Schroeter, Kesseler, Liesche, and Müller), A., i, 146.

4:4′-Dimethoxydi-*α*-naphthyl diketone (Giua), A., i, 204.

4:4′-Dimethoxydi-*α*-naphthyl ketone (Giua), A., i, 204.

2:2′-Dimethoxydiphenyl, 5:5′-*di*- and 3:5:3′:5′-*tetra*-nitro- (Borsche and Scholten), A., i, 391.

Dimethoxydistyryl ketones, additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 208.

4:5-Dimethoxy-1-methyl-4:5-dihydrouric acid (Biltz and Strufe), A., i, 293.

o-**1:6-Dimethoxy-2-naphthoylbenzoic acid**, and its methyl ester (Fischer and König), A., i, 661.

2:5-Dimethoxy-*β*-nitro-Δ^{α}-propenylbenzene (Kauffmann, Burr, Meyer, and Jeutter), A., i, 392.

1:2-Dimethoxyphenanthraphenazine, 4-bromo- (Jones and Robinson), T., 928.

2:5-Dimethoxy-*α*-phenylcinnamic acid (Kauffmann, Burr, Meyer, and Jeutter), A., i, 392.

"**Dimethoxysaccharin.**" See Veratricsulphinide.

pp′-**Dimethoxystilbene**, additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 207.

2:5-Dimethoxystilbene, ω-nitro-(Kauffmann, Burr, Meyer, and Jeutter), A., i, 392.

2:5-Dimethoxystyrene, ω-nitro- (Kauffmann, Burr, Meyer, and Jeutter), A., i, 392.

4:5-Dimethoxy-1:3:7:9-tetramethyl-4:5-dihydrouric acid (Biltz and Strufe), A., i, 300.

4:5-Dimethoxy-1:3:7-trimethyl-9-ethyl-4:5-dihydrouric acid (Biltz and Bergius), A., i, 589.

4:5-Dimethoxy-3:7:9-trimethyl-1-ethyl-4:5-dihydrouric acid (Biltz and Max), A., i, 590.

Dimethylacetonedicarboxylic acid, esters of, and their derivatives (Schroeter, Kesseler, Liesche, and Müller), A., i, 146.

2:7-Dimethylacridine, 3:6-*di*amino-, cadmium and silver compounds, preparation of (Soc. Chem. Ind. Basle), A., i, 582.

1:6- and 3:8-Dimethylallantoins (Biltz, Heyn, and Bergius), A., i, 291.

Dimethylamine, preparation of (Werner), T., 844; A., i, 632.
  physical constants of (Berthoud), A., ii, 237.

o-**Dimethylamino***iso***amylbenzene**, and its salts (v. Braun, Heider, and Neumann), A., i, 168.

2:4-Dimethylaminoanisole, 3:5-*di*nitro-(Hindmarsh, Knight, and Robinson), T., 944.

p-**Dimethylaminobenzanilide** (Staudinger and Endle), A., i, 646.

p-**Dimethylaminobenz-azide** and **-hydrazide** (Staudinger and Endle), A., i, 666.

p-**Dimethylaminobenzhydryl(diphenyl-*p*-diethylaminobenzyl)benzene** (Pérard), A., i, 651.

p-**Dimethylaminobenzhydryl(diphenyl-*p*-dimethylaminobenzyl)benzene** (Pérard, A., i, 651.

p-**Dimethylaminobenzylidenedeoxybenzoin** (Kauffmann, Burr, Meyer, and Jeutter), A., i, 392.

p-**Dimethylaminobenzoyl** chloride (Staudinger and Endle), A., i, 646.

ζ-**Dimethylamino-γ-benzoyl-γ-ethylhexane**, and its platinichloride (Haller and Ramart-Lucas), A., i, 665.

ζ-**Dimethylamino-γ-benzoyl-γ-methylhexane**, and its salts (Haller and Ramart-Lucas), A., i, 665.

ε-**Dimethylamino-β-benzoyl-β-methylpentane**, and its derivatives (Haller and Ramart-Lucas), A., i, 665.

p-**Dimethylaminobenzylbenzopinacone** (Pérard), A., i, 652.

p-**Dimethylaminobenzylbenzoylbenzene** (Pérard), A., i, 653.

p-**Dimethylaminobenzyltriphenylcarbinol**, and its derivatives (Pérard), A., i, 652.

δ-**Dimethylaminobutan-β-one**, salts of (Mannich), A., i, 634.

γ-**Dimethylaminobutylbenzene**, and its salts (v. Braun and Neumann), A., i, 282.

Dimethylaminocodide, and its platinichloride (v. Braun and Kindler), A., i, 164.

Dimethylaminocyanonorcodide, and its salts (v. Braun and Kindler), A., i, 164.

p-**Dimethylamino-ω-cyanostilbene** (Kauffmann and Meyer), A., i, 395.

3-Dimethylamino-9:9(or 10:10)-dimethylaminodiphenylanthrone (Pérard), A., i, 653.

αε-**Dimethylamino-βδ-dimethylpentan-γ-one** (Mannich), A., i, 635.

3-Dimethylamino-9:10-diphenylanthracene (Pérard), A., i, 653.

p-**Dimethylaminodiphenylcarbamide** (Staudinger and Endle), A., i, 667.

3-Dimethylamino-9:10-diphenyldihydroanthracene (Pérard), A., i, 653.

pp'-**Dimethyl*di*aminodi-*o*-tolyl ketone**, and *di*cyano-, and *di*nitroso- (v. Braun), A., i, 175.

pp'-**Dimethyl*di*aminodi-*o*-tolylmethane**, and its derivatives (v. Braun), A., i, 174.

Dimethylamino-*N*-β-hydroxyethylnorcodide, and its platinichloride (v. Braun and Kindler), A., i, 164.

3-Dimethylamino-9-*p*-hydroxyphenyl-6-dimethylfluorime (Ghosh and Watson), T., 827.

3-Dimethylamino-9-*op*-*di*hydroxyphenyl-6-dimethylfluorime, and its benzoyl derivative (Ghosh and Watson), T., 827.

α-**Dimethylamino-β-methylpentan-γ-one**, and its salts (Mannich), A., i, 635.

ββ-**Dimethylaminomethylpentan-γ-one**, and its salts (Mannich), A., i, 635.

Dimethylaminonorcodide, and its salts (v. Braun and Kindler), A., i, 164.

Dimethylaminophenonaphthazoxone (Kehrmann and Herzbaum), A., i, 593.

p-**Dimethylaminophenylcarbamic acid**, methyl ester (Staudinger and Endle), A., i, 667.

p-**Dimethylaminophenylcarbimide** (Staudinger and Endle), A., i, 667.

o-**Dimethylaminophenyl*cyclo*hexane,** and its salts (v. Braun, Heider, and Neumann), A., i, 168.

3-Dimethylamino-9(or **10**)**-phenyloxanthranol,** and its derivatives (Pérard), A., i, 653.

p-**Dimethylaminophenylurethane.** See *p*-Dimethylaminophenylcarbamic acid, methyl ester.

o-**Dimethylaminopropylbenzene,** and its derivatives (v. Braun, Heider, and Neumann), A., i, 168.

β-**Dimethylaminopropylbenzenes,** and their methiodides (v. Braun, Heider, and Neumann), A., i, 168.

4′-Dimethylaminostilbene-4-carboxylic acid, 2-nitro-, and its salts (Pfeiffer, Klinkert, and v. Pollitzer), A., i, 141.

5-Dimethylamino-ψ-uric acid (Biltz and Heyn), A., i, 288.

Dimethylammonium palladichloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.

Dimethylaniline, condensation of ethylene dibromide and (v. Braun and Arkuszewski), A., i, 175.
  additive compound of, with 2.4:6-trinitrostilbene (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 208.

2:3-Dimethylbenzopyrone, bromo-derivatives of (Simonis and Herovici), A., i, 409.

3:6-Dimethyl-1:4-benzopyrone (v. Auwers), A., i, 277.

Dimethyl*cyclo*butane-1:3-dione, derivatives of (Schroeter, Kesseler, Liesche, and Müller), A., i, 149.

1:3-Dimethyl*cyclo*butane-2:4-dione-1-carboxylic acid, esters of (Schroeter, Kesseler, Liesche, and Müller), A., i, 146.

1:3-Dimethyl*cyclo*butane-2:4-dionedicarboxylic acid, methyl ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 148.

1:3-Dimethyl-5-*tert*.-butylbenzene, 2:4:6-*tri*amino- (Herzig, Wenzel, and Kichler), A., i, 177.

α-*p*-**Dimethylcinnamic acid,** and its methyl ester (v. Auwers), A., i, 267.

β-**Dimethylcinnamic acids,** stereoisomeric, and their derivatives (Stoermer, Grimm, and Laage), A., i, 648.

4:7-Dimethylcoumarin periodide (Simonis), A., i, 706.

2:4′-Dimethyldiaminophenyl *m*-**tolyl ketone,** and 2:4′-*di*cyano-, and their derivatives (v. Braun, A., i, 174.

2:4′-Dimethyldiaminophenyl-*m*-tolylmethane, and its derivatives (v. Braun), A., i, 174.

3:8-Dimethyl-1:6-diethylallantoin (Biltz and Max), A., i, 590.

s-**Dimethyldiethylalloxantin** (Biltz and Max), A., i, 591.

1:4-Dimethyl-2:5-diethylbenzene (Freund, Fleischer, and Gofferjé), A., i, 575.

Dimethyldiethylbutinenediol. See γζ-Dimethyl-Δ^{δ}-octinene-γζ-diol.

1:9-Dimethyl-3:7-diethyl*spiro*-5:5-dihydantoin (Biltz and Max), A., i, 590.

4:7-Dimethyl-2:2-diethyl-1:3-diketohydrindene-5:6-dicarboxylic acid (Freund, Fleischer, and Gofferjé), A., i, 573.

3:7-Dimethyl-1:9-diethyluric acid (Biltz and Max), A., i, 590.

4:4′-Dimethyl-1:1′-dithioxanthonyl (Ullmann and v. Glenck), A., i, 161.

Dimethylenedioxydistyryl ketone, additive compound of stannic chloride and (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 208.

Dimethylenegluconic acid, behaviour of, in the organism (Paderi), A., i, 716.

2:3:6:7-Dimethylenetetraoxyanthraquinonedi-imide (Brown and Robinson), T., 957.

4:5:4′:5′-Dimethylenetetraoxyazobenzene (Robinson), T., 113.

4:5:4′:5′-Dimethylenetetraoxyazoxybenzene-2′-carboxylic acid, 2-nitro- (Robinson), T., 119; A., i, 227.

Dimethylenetetraoxydistyryl ketone, 6′-*di*chloro- (Orr, Robinson, and Williams), T., 948.

5:6:4′:5′-Dimethylenetetraoxy-2-phenylindazole-2′-carboxylic acid, 3-hydroxy-, lactone of (Robinson), T., 118; A., i, 227.

Dimethylerythrene, polymerisation of (Ostromisslenski), A., i, 399.

1:6-Dimethyl-3-ethylallantoin (Biltz and Max), A., i, 591.

1:4-Dimethyl-2-ethylbenzene (Freund, Fleischer, and Gofferjé), A., i, 573.

1:3-Dimethyl-7-ethylcaffolide (Biltz and Max), A., i, 590.

1:7-Dimethyl-3-ethylcaffolide (Biltz and Bergius), A., i, 589.

2:5-Dimethyl-4-ethylphenyl methyl ketone, and its semicarbazone (Freund, Fleischer, and Gofferjé), A., i, 574.

3:7-Dimethyl-1-ethyluric acid, preparation and derivatives of (BILTZ and MAX), A., i, 590.
3:7-Dimethyl-1-ethyl-$\Delta^{4:9}$-*iso*uric acid, 5-chloro- (BILTZ and MAX), A., i, 591.
2:5-Dimethylfuran-3:4-dicarboxylic acid, ethyl ester, hydrolysis of (KORSCHUN and GOUNDER), A., i, 91.
4:5-Dimethylglyoxalone, preparation of (JOHNSON and HADLEY), A., i, 585.
1:9- and **3:7-Dimethyl*spiro*-5:5-hydantoins** (BILTZ, HEYN, and BERGIUS), A., i, 291.
1:3-Dimethylhydantoylethylamide, and 5-hydroxy- (BILTZ and MAX), A., i, 590.
1:2-Dimethylhydrindene, 1-hydroxy-. See 1:2-Dimethylindan-1-ol.
Di-2-methyl-2-hydrindylthiocarbamide (v. BRAUN, KRUBER, and DANZIGER), A., i, 132.
Dimethyl-γ-hydroxypropylallylammonium chloride. See Allylhomocholine chloride.
1:2-Dimethylindan-1-ol (STOERMER and LAAGE), A., i, 654.
2:3-Dimethylindene, and its picrate (STOERMER and LAAGE), A., i, 655.
1:2-Dimethylinden-1-ol (STOERMER and LAAGE), A., i, 654.
Di-2-methyl-3-indolyl ether (BAUDISCH and HOSCHEK), A., i, 166.
Di-3-(2-methylindolyl)-*o*-aminophenylmethane, and its hydrochloride and acetyl derivative (HOSCHEK), A., i, 167.
γζ-Dimethyloctane-γζ-diol, and its derivatives (ZALKIND and MARKARJAN), A., i, 114.
γζ-Dimethyl-Δ^{δ}-octene-γζ-diol, and its derivatives (ZALKIND and MARKARJAN), A., i, 114.
γζ-Dimethyl-Δ^{δ}-octinene-γζ-diol, hydrogenation of (ZALKIND and MARKARJAN), A., i, 113.
2:5-Dimethylolpyrrole (TSCHELINCEV and MAKSOROV), A., i, 165.
1:4-Dimethyl*cyclo*pentadienedihydropyridazine, 6-nitro- (HALE), A., i, 55.
1:2-Dimethyl*cyclo*pentane, 1-nitro- (ROZANOV), A., i, 133.
1:1-Dimethyl*cyclo*pentane-3-one-2-carboxylic acid, 2-cyano-, ethyl ester, derivatives of (NOYES and MARVEL), A., i, 455.
1:1-Dimethyl*cyclo*pentane-3-oxime, 2-cyano-, and its 2-carboxylic acid (NOYES and MARVEL), A., i, 455.
2:5-Dimethylphenol, 4-amino-, acetyl derivative (JACOBS and HEIDELBERGER), A., i, 696.
2:5-Dimethylphenoxyacetic acid, 4-amino-, and its derivatives (JACOBS and HEIDELBERGER), A., i, 696.
2:6-Dimethylpiperidines, substituted, preparation of (JUDD and KON), A., i, 282.
αα-Dimethylpropionoylsemicarbazide (BOUGAULT), A., i, 689.
3:6-Dimethylpyridazine-4:5-dicarboxylic acid, and its silver salt (HALE), A., i, 55.
β-1:6-Dimethylpyridyl-2-ethyl alcohol, and its acetate (HESS, UIBRIG, and EICHEL), A., i, 351.
4:8-Dimethyl-2:2:6:6-tetraethyl-3-hydrindacene (FREUND, FLEISCHER, and GOFFERJÉ), A., i, 573.
4:8-Dimethyl-2:2:6:6-tetraethyl-*s*-hydrindacene-1:3-dione (FREUND, FLEISCHER, and GOFFERJÉ), A., i, 573.
***meso*-2:5-Dimethyltetrahydrothiophen,** and its derivatives (GRISCHKEVITSCH-TROCHIMOVSKI), A., i, 155.
3:5-Dimethyltetrahydrothiophen-2-carboxylic acid, and its silver salt (GRISCHKEVITSCH-TROCHIMOVSKI and GALPERIN), A., i, 156.
Dimethylthiazine, and its salts (KEHRMANN, ROBERT, and SANDOZ), A., i, 226.
Dimethylthiophen mercuri-haloids (STEINKOPF), A., i, 303.
3:5-Dimethylthiophen, 2-iodo- (GRISCHKEVITSCH-TROCHIMOVSKI and GALPERIN), A., i, 155.
Dimethyl-*o*-toluidine, condensation of trioxymethylene and (v. BRAUN and HEIDER), A., i, 175.
Dimethyl-*p*-toluidine, 2:3-*di*nitro- (JANSEN), A., i, 128.
Dimethyl-*o*-toluidinium palladochloride (GUTBIER, FELLNER, KRÄUTER, FALCO, KRELL, SCHULZ, and WOERNLE), A., i, 541.
4:3-Dimethyl-2:2:5-triethyl-1:3-diketohydrindene (FREUND, FLEISCHER, and GOFFERJÉ), A., i, 573.
4:7-Dimethyl-2:2:5-triethylhydrindene (FREUND, FLEISCHER, and GOFFERJÉ), A., i, 573.
2:4-Dimethyltrimethylene sulphide, and its derivatives (GRISCHKEVITSCH-TROCHIMOVSKI), A., i, 154.
7:7-Dimethyluramil (BILTZ and HEYN), A., i, 288.
1:3-Dimethyl-ψ-uric acid, 5-chloro- (BILTZ and STRUFE), A., i, 297.
1:7-Dimethyl-ψ-uric acid, 5-chloro- (BILTZ and DAMM), A., i, 295.
1:3-Dimethyl-$\Delta^{4(9)}$-*iso*uric acid, 5-chloro- (BILTZ and STRUFE), A., i, 296.
1:7-Dimethyl-$\Delta^{4(9)}$-*iso*uric acid, 5-chloro- (BILTZ and DAMM), A., i, 294.

Di-α-naphthyl telluride, and its salts (Lederer), A., i, 134.
Dinaphthylsulphones, *di*hydroxy- (Hinsberg), A., i, 576.
Dindole (Ruggli), A., i, 587; (Heller), A., i, 708.
2:6-Dinitratomercurithymol (Rupp), A., i, 670.
Dioptase from Traversella (Colomba), A., ii, 377.
Di-*o*- and -*p*-phenetyl tellurides, and their salts and derivatives (Lederer), A., i, 134, 264.
3:3′-Diphenol, amino-, bromo-, and nitro-derivatives of (Borsche), A., i, 558.
Diphenyl, and its derivatives, crystallography of (Mieleitner), A., i, 641.
*di*sulphide, *di*-2-nitro-*di*-4-cyano- (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 17.
Diphenyl, 2:5:2′:5′: *tetra*chloro- (Meyer and Hofmann), A., i, 642.
chloronitro- and nitroamino-derivatives of (Borsche and Scholten), A., i, 390.
αγ-**Diphenylacetoacetic acid,** methyl ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 146.
Diphenylacetonedicarboxylic acid, methyl ester (Staudinger and Hirzel), A., i, 631.
Diphenylamine, preparation of (Flürscheim), A., i, 330.
use of, in colorimetric estimations (Smith), A., ii, 217.
Diphenylamine, 2-amino-4-cyano- (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 16.
nitrohydroxy-derivatives (Meldola, Foster, and Brightman), T., 546; A., i, 454.
Diphenylaminotetramethylammonium (Schlenk and Holtz), A., i, 263.
1:5 Diphenyl-3-anisylpyrazole (Jörlander), A., i, 223.
Diphenyl-*p*-azophenylene, *tetra*amino-, and its salts and derivatives (Heidtschka and Goldstein), A., i, 482.
Diphenylbenzidine, use of, in colorimetric estimations (Smith), A., ii, 217.
2:6-Diphenyl-3-benzylidene-5:5-dimethyltetrahydropyrone (H. and P. Ryan), A., i, 348.
αγ-**Diphenyl-β-benzylidenepropane,** and αβ-*di*bromo- (Orechov and Grinberg), A., i, 450.
Diphenyl-*p*-bromophenylmethylhydroxylamine, and its hydrochloride (Stagner), A., i, 24.
β-Diphenyl-*p*-bromophenylmethyl-β-methylhydroxylamine (Stieglitz and Stagner), A., i, 23.
Diphenylbutadiene (Johlin), A., i 329.
Diphenylcarbinols, action of aromatic sulphinic acids with (Hinsberg), A., i, 328.
Diphenyl-*p*-chlorophenylmethylamine, and its salts (Vosburgh), A., i, 21.
Diphenyl-*p*-chlorophenylmethyl*di*chloroamine (Vosburgh), A., i, 21.
Diphenyl*tetra*chlorophthalide (Orndorff and Murray), A., i, 338.
γδ-Diphenyl-αζ-dianisylhexane-αζ-dione (Jörlander), A., i, 343.
Diphenyldi-*n*-butyltetrazone (Reilly and Hickinbottom), T., 1030.
2:2-Diphenyl-1:1-di(-*p* diethylaminophenyl)-1:2-dihydro*iso*benzofuran (Pérard), A., i, 652.
2:2-Diphenyl-1:1-di(-*p*-dimethylaminophenyl)-1:2 dihydro*iso*benzofuran (Pérard), A., i, 651.
3:5 Diphenyl-4:5-dihydro*iso*oxazoles, 4- and 5-hydroxy- (Widman), A., i, 221.
3:5′-Diphenyldihydro-1:2-triazolotriazole, 5:3′-*di*hydroxy-, and its derivatives (Bailey and Moore), A., i, 355.
5:3′-*di*thiol- (Bailey and McPherson), A., i, 588.
2:2-Diphenyl-1-*p*-dimethylaminophenyl-1-*p*-diethylaminophenyl-1:2-dihydro*iso*benzofuran (Perard), A., i, 651.
Diphenyldipyruvic acid, esters of (Hemmerlé), A., i, 394.
2:2′-Diphenyldiquinone-4:4′ dioxime (Borsche and Scholten), A., i, 390.
Diphenylene oxide, 1:3:6:8-*tetra*nitro- (Borsche and Scholten), A., i, 390.
s-**Diphenylethane,** 3:3′-*di*fluoro- (Meyer and Hofmann), A., i, 642.
αα-**Diphenylethylamine,** and its nitrite (Brander), A., i, 555.
αα-**Diphenylethylcarbamic acid,** ethyl ester (Brander), A., i, 560.
αα-**Diphenylethylcarbamide** (Brander), A., i, 556.
αα-**Diphenylethyloxamic acid,** ethyl ester (Brander), A., i, 555.
αα-**Diphenylethyloxamide** (Brander), A., i, 555.
Diphenylglycollic azide, and its derivatives (Curtius and Goldberg), A., i, 637.
Diphenylglycollohydrazide, and its derivatives (Curtius and Goldberg), A. i, 637.
Diphenylhydroxyacetic acid, *p*-nitrobenzyl ester (Lyons and Reid), A., i, 559.

Diphenylindene, synthesis of (Orechov), A., i, 450.
1:2- and **2:3-Diphenylindenes** (Ruggli), A., i, 551.
Diphenyliodonium chloride, crystallography of (van der Veen), A., i, 548.
Diphenylmethane, 3:6:3′:6′-*tetra*hydroxy-, preparation of (Ghosh and Watson), T., 825.
Diphenylmethanedimethyldihydrazine, action of, on sugars (v. Braun), A., i, 251.
Diphenylmethylammonium palladochloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.
Diphenylmethyl α-naphthyl sulphone (Hinsberg), A., i, 329.
Diphenylmethyloxalacetic acid. See α-Oxalo-ββ-diphenylpropionic acid.
1:3-Diphenyl-5-*m*-nitrophenylpyrazole (Bodforss), A., i, 225.
1:3-Diphenyl-5-*m*-nitrophenylpyrazoline, and 4-hydroxy- (Bodforss), A., i, 225.
1:4-Diphenyl*cyclo*pentadienedihydropyridazine, 6-nitro- (Hale), A., i, 56.
Di-α-phenyl*iso*propyloxamide (Brander), A., i, 555.
3:5-Diphenylpyrazoline, 4-hydroxy-, and its nitroso-derivative (Widman), A., i, 222.
2:6-Diphenylpyryl ferrichloride (Dilthey), A., i, 661.
2:3-Diphenylquinoxaline, 6-cyano- (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 17.
Diphenylsuccinic acids, *l*-menthyl esters of (Wren and Still), T., 513; A., i, 456.
r- and *meso*-**Diphenylsuccinic acids**, interconversion of the esters of (Wren and Still), T., 1019.
2:3-Diphenylthiohydantoin, 2:3-*di-p*-hydroxy- (Stieger), A., i, 173.
Diphenylthioparabanic acid, *di-p*-hydroxy- (Stieger), A., i, 172.
2:6-Diphenyl-1-*m*-tolylpiperid-4-one (Mayer), A., i, 144.
3:4-Diphenyltriazole, 5-hydroxy- (Bailey and McPherson), A., i, 587.
Dipiperidinotetraminoarsenobenzene hydrochloride (Farbwerke vorm. Meister, Lucius, and Brüning), A., i, 359.
"**Dipronal.**" See α-Propylvalerylurethane.
Dipropionyl-*l*-cystine, *di-d-* and *l*-α-bromo- (Abderhalden and Wybert), A., i, 120.
Di*iso*propylacetonedicarboxylic acid, ethyl ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 146.
Dipropylammonium palladichloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 542.
Disaccharides, constitution of (Haworth and Law), A., i, 80.
Disinfectants, use of mercury organic compounds as (Schrauth and Schoeller), A., i, 241.
Dispersion, rotatory (Patterson), A., ii, 4, 5.
Dissociation of double salts in aqueous solution (Maxwell), A., ii, 562.
Dissociation pressure of sulphides (Allen and Lombard), A., ii, 194.
Distillation in steam (Richmond), A., i, 316; (Tromp), A., ii, 193.
  of aliphatic acids (Upson, Plum, and Schott; Lamb; Richmond), A., ii, 277.
Distillation apparatus (Stearns), A., ii, 567.
  for manipulation of small quantities of volatile substances (Stock), A., ii, 442.
  vacuum (Duschak and Spencer), A., ii, 316.
p-**Distyrylbenzene**, and ωω′-*di*cyano- (Kauffmann and Jeutter), A., i, 395.
3:5′-Distyryldihydro-1:2-triazolotriazole, 5:3′-*di*hydroxy- (Bailey and McPherson), A., i, 588.
Disuccinyl*di-o*-aminotolane, *di-o′*-nitro- (Ruggli), A., i, 22.
βδ-**Disulphohexoic acid**, and its derivatives (Nottbohm), A., i, 29.
2:5-Di-*o*-sulphophenyl-1:3:4-triazole, 1-amino- (Schrader), A., i, 710.
βδ-**Disulpho-δ-phenylvaleric acid**, and its derivatives (Nottbohm), A., i, 28.
βδ-**Disulphovaleric acid**, and its derivatives (Nottbohm), A., i, 28.
Dithienylchloroarsine (Steinkopf and Bauermeister), A., i, 303.
2:2′-Di-*p*-toluenesulphonoxyazoxybenzene (Baudisch and Haftka), A., i, 357.
Di-*p*-tolylaminotetramethylammonium (Schlenk and Holtz), A., i, 262.
Ditolyl*tetra*chlorophthalide (Orndorff and Murray), A., i, 338.
Ditriphenylmethyloxamide (Brander), A., i, 555.
Divinyl, polymerisation of (Ostromisslenski), A., i, 399.
Dogs, pancreatic diabetes in (Murlin and Kramer; Kramer, Marker, and Murlin; Murlin, Kramer, and Riche), A., i, 69.

Dogs, effect of hydrochloric acid on the excretion of metallic salts in (Stehle), A., i, 609.
  utilisation of inositol by (Greenwald and Weiss), A., i, 610.
  influence of inositol on the excretion of phenol by (Dubin), A., i, 187.
Dog-fish. See *Scyllium canicula.*
Dolomite from Kielce, Poland (Thugutt), A., ii, 488.
Dopamelanin (Bloch), A., i, 675.
Dopaoxydase (Bloch), A., i, 675.
Drop weights, measurement of surface tension by means of (Perrot), A., ii, 408.
Droseraceæ, microchemistry of (Fünfstück and Braun), A., i, 506.
Drosera rotundifolia, proteoclastic enzymes of (Dernby), A., i, 506.
Drosophila, use of yeast in nutrition of (Northrop), A., i, 525.
Durene, additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 207.
  effect of, on the olfactory organ (Backman), A., i, 498.
Dugong, Australian, oil from (Challinor and Penfold), A., i, 239.
Dyeing, theory of (Sisley), A., ii, 527.
  of cotton fibres (Haller), A., i, 436.
Dye liquors, estimation of sodium sulphide in (Swann), A., ii, 385.

E.

Eakleite (Larsen), A., ii, 417.
Earths, rare, compounds of (Grant and James), A., ii, 316.
  separation of (Engle and Balke), A., ii, 259.
Ebullioscope, improved (Smits), A., ii, 66.
Eggs, yolk of, supposed existence of lecithin in (Barbieri), A., i, 238.
  Chinese preserved (Blunt and Wang), A., i, 102.
  echinoderm, cytolysis in (Moore), A., i, 493.
  sea-urchin, cytolysis in (Moore), A., i, 185.
Electric discharge through gases (Wright), T., 643; A., ii, 403.
Electrical conductivity, measurement of (Washburn), A., ii, 10; (Washburn and Parker), A., ii, 235.
  water correction in determination of (Kendall), A., ii, 234.
  and chemical constitution (Fink), A., ii, 163.
  of salts of organic acids (Thoms and Zehrfeld), A., i, 699.
Electrical conductivity, metallic salts in pyridine (Mathews and Johnson), A., ii, 289.
  of solutions (Taylor and Acree), A., ii, 7, 8.
Electrical osmosis (Briggs), A., ii, 236.
Electro-capillary function (Gouy), A., ii, 291.
Electrode, chromic-chromous, oxidation potential of (Forbes and Richter), A., ii, 353.
  ferro-ferricyanide, electromotive force measurements with (Linhart), A., ii, 233.
  hydrogen, potential of (Loomis and Acree), A., ii, 12; (Loomis, Myers, and Acree), A., ii, 289.
  lead, potential of (Lewis and Brighton), A., ii, 524.
  mercury, potential measurements with (Linhart), A., ii, 13.
  mercurous chloride (*calomel*), potential measurements with (Loomis and Meacham), A., ii, 13.
  potassium chloride in hydrochloric acid, potential of (Loomis, Essex, and Meacham), A., ii, 353.
  silver, potential of (Mortimer and Pearce), A., ii, 289.
  for titration of gastric juice (Michaelis), A., ii, 228.
Electrolysis (Muller), A., ii, 117.
  with alternating currents (Ríus y Miró), A., ii, 291.
Electrolytes, difference of potential due to movement of (Kruyt), A., ii, 403.
  concentration of, round the electrodes (Procopiu), A., ii, 291.
  permeability of red blood-corpuscles to (Rohonyi; Rohonyi and Lóránt), A., i, 235.
  diffusion of, through living cells (Loeb), A., i, 66, 67, 102.
Electrolytic analysis. See Analysis.
  dissociation, theory of (de Szyszkowski), A., ii, 127.
    abnormal (Sachanov), A., ii, 234.
    of metallic salts (Sachanov), A., ii, 115.
  diazotisation (Krauss), A., i, 518.
Electromotive equilibria and allotropy (Smits and Aten), A., ii, 232.
Electromotive force, measurements of, with the ferro-ferricyanide electrode (Linhart), A., ii, 233.
  of non-aqueous cells (Nelson and Evans), A., ii, 232.
Electron conception of valency (Spiegel), A., ii, 28.
Electrons, mobility of, in gases (Wellisch), A., ii, 352.

Elements, structure and evolution of (Harkins), A., ii, 303.
  spectra of, and the periodic system (Kütter), A., ii, 185.
  periodic system of (Silbermann), A., ii, 27.
  a third state of (Hering), A., ii, 460.
  chemical, conception of (Fajans), A., ii, 566.
  isotopic, atomic weight determination and solubility of salts of (Fajans and Fischler; Fajans and Lembert), A., ii, 472.
    Rontgen ray spectra of (Siegbahn and Stenström), A., ii, 524.
Emetamine and its salts (Pyman), T., 442; A., i, 410.
*iso***Emetine**, and its derivatives (Karrer), A., i, 410.
Emodin, identification of drugs containing (Beal and Okey), A., ii, 279.
Emulsification, theories of (Roon and Oesper), A., ii, 299.
Emulsions, solvent properties of (Sisley), A., ii, 527.
Energy and heat capacity (Bell; Richards), A., ii, 65.
Entropy, relation of heat capacity to (Njegovan), A., ii, 405.
Enzymes, formation of (Jacoby), A., i, 71, 106, 305, 430, 528.
  chemical composition and formation of (v. Euler and Griese), A., i, 679.
  optical activity of (Rakuzin), A., ii, 286.
  periodicity of the action of (Groll), A., i, 425.
  poisoning of, in living cells (H. v. and B. Euler), A., i, 72.
  inhibition of the action of, by urine (v. Euler and Svanberg), A., i, 676.
  in blood (Satta), A., i, 100.
  of human cerebro-spinal fluid (Leschke and Pincussohn), A., i, 363.
  glycolytic (Lombroso), A., i, 182.
  proteoclastic, of yeast (Dernby), A., i, 500.
  proteolytic, measurement of the action of (Sherman and Neun), A., ii, 111.
  reducing, non-specificity of (Bach), A., i, 375, 431; (Abelous and Aloy), A., i, 618.
  of the spleen (Morse), A., i, 606.
  of yeast (Neuberg and Färber; Harden), A., i, 501.
Enzymes. See also:—
  Achroodextrinase.
  Amylase.
  Arginase.
Enzymes. See also:—
  Catalase.
  Diastase.
  Dopaoxydase.
  Erepsin.
  Ereptase.
  Esterase.
  β-Galactosidase.
  β-Glucosidase.
  Invertase.
  Lipase.
  Oxydase.
  Pancreatin.
  Pepsin.
  Peroxydase.
  Ptyalin.
  Saccharophosphatase.
  Thrombin.
  Trypsin.
  Tyrosinase.
  Urease.
  Zymin.
Enzyme action (Falk), A., i, 182, 598; (van Slyke and Cullen), A., i, 182; (Abderhalden and Fodor), A., i, 306; (Frankel), A., i, 597.
"**Epronal.**" See α-Ethylvalerylurethane.
Equation, Dieterici's (MacDougall), A., ii, 366.
  of state, values of *b* and $\sqrt{a}$ in the (van Laar), A., ii, 67.
    Kamerlingh Onnes (Bakker), A., ii, 16.
Equilibria, non-, uni-, and bi-variant (Schreinemakers), A., ii, 132, 169, 195, 247, 299, 411, 454.
  chemical, effect of temperature on (Scheffer), A., ii, 170.
Equilibrium in binary systems (Kruyt and Heldermann; Voano), A., ii, 81; (Kruyt), A., ii, 133.
  of a system under the influence of an external agent (Volchonski), A., ii, 133.
  in solutions, influence of the solvent on (Smits), A., ii, 171.
Equilibrium constant, effect of pressure on the (Lewis), A., ii, 456.
Erbium, arc spectra of (Eder), A., ii, 1.
Erepsin (Dernby), A., i, 234.
Ereptase (Dernby), A., i, 234.
  hydrolysis of glycylglycine by (Dernby), A., ii, 82.
Erucic acids, isomerism of brassidic acid and (Mascarelli), A., i, 195.
Eruco-*p*-ethoxyanilide (de' Conno), A., i, 388.
Eruco-*p*-hydroxyanilide (de' Conno), A., i, 388.
Eruco-*p*-methoxyanilide (de' Conno), A., i, 388.

Eruco-α- and -β-naphthalides (de Conno), A., i, 388.

Eruco-*p*-phenylenediamide (de Conno), A., i, 389.

Eruco-*p*-toluidide (de Conno), A., i, 387.

Eruco-*m*-xylidide (de Conno), A., i, 387.

Erythrodextrin, digestion of, by ptyalin (Blake), A., i, 361.

Esterases, distribution of, in the animal organism (Porter), A., i, 238.

Esters, preparation of (Boiteau), A., i, 2.
  formation of (McIntosh), A., i, 441.
  reactions of, with magnesium organic compounds (Stadnikov), A., i, 136.

Esterification (Kimball and Reid), A., i, 88; (Sachs and Reid), A., i, 89; (Faber and Reid), A., i, 626.

Ethane, *tetra*- and *hexa*-chloro-, ultraviolet absorption spectra of (Massol and Faucon), A., ii, 188.

Ethers, compounds of metallic haloids with, and their decomposition products (Coney), A., i, 135.

Ethers, chloro- (Clark, Cox, and Mack), A., i, 316.

α-**Ethoxalylcrotonic acid,** β-amino-, and its copper salt (Benary, Reiter, and Soenderop), A., i, 253.

Ethoxide, lithium, potassium and sodium, velocity of reaction of methyl iodide with (Brown and Acree), A., ii, 24.
  inversion of *l*-menthone by (Gruse and Acree), A., ii, 251.

Ethoxyacetic acid, ethyl ester, hydrazide of, and its derivatives (Curtius and van der Laan), A., i, 635.

Ethoxyacetylazide (Curtius and van der Laan), A., i, 636.

Ethoxybenzene, 3:5-*di*nitro-2:4-*di*amino-β-hydroxy-, and its β-benzoyl derivative and 3:5-*di*nitro-2:4:β-*tri*hydroxy- (G. M. and R. Robinson), T., 936.

Ethoxycrotonic acid, ethyl ester, condensation of ethyl oxalate with (Wislicenus and Schöllkopf), A., i, 700.

Ethoxydihydroberberine (G. M. and R. Robinson), T., 968.

5-**Ethoxy-1:3-dimethyl-4:5-dihydrouric acid,** 4-hydroxy- (Biltz and Strufe), A., i, 297.

5-**Ethoxy-1:3-dimethyl-$\Delta^{4(9)}$-*iso*uric acid** (Biltz and Strufe), A., i, 296.

Ethoxyethylaminoformylchloride (Jones and Neuffer), A., i, 325.

3-**Ethoxy-1-ethyltheobromine** (Biltz and Max), A., i, 590.

5-**Ethoxy-3:9-methyl-4:5-dihydrouric acid,** 4-hydroxy- (Biltz and Strufe), A., i, 294.

5-**Ethoxy-9-methyl-4:5-dihydrouric acid,** 4-hydroxy- (Biltz and Heyn), A., i, 292.

Ethoxymethylurethane (Curtius and van der Laan), A., i, 636.

5-**Ethoxy-1-methyl-ψ-uric acid** (Biltz and Strufe), A., i, 294.

5-**Ethoxy-9-methyl-ψ-uric acid** (Biltz and Heyn), A., i, 292.

1:4-**Ethoxynaphthoic acid,** structure of (Kamm, McClugage, and Landstrom), A., i, 455.

α-**Ethoxynaphthoylformic acid.** See α-Ethoxynaphthylglyoxylic acid.

Ethoxy-β-naphthoylpropionic acid (Giua), A., i, 394.

α-**Ethoxynaphthylglyoxylic acid** (Kamm, McClugage, and Landstrom), A., i, 455.

2-**Ethoxy-$\Delta^{1:3}$-*cyclo*pentadien-5-one-1-carboxylic acid,** 4-hydroxy-, ethyl ester, potassium salt (Wislicenus and Schöllkopf), A., i, 701.

2-**Ethoxyphenol,** 4- and 5-nitro-, and their benzoates (G. M. and R. Robinson), T., 933.

α-**Ethoxyphenylacetic acid,** methyl ester, amide and nitrile of (Hess and Dorner), A., i, 337.

Ethoxyphenyltartramic acid, and its esters and amide (Casale), A., i, 643.

p-**Ethoxyphenyltartrimide** (Casale), A., i, 643.

Ethoxypropene, condensation of ethyl oxalate with (Wislicenus and Schöllkopf), A., i, 700.

4-**Ethoxy-α-pyrone-6-carboxylic acid,** and its potassium salt and ethyl ester (Wislicenus and Schöllkopf), A., i, 701.

6-**Ethoxy-1:2-pyrone-3-carboxylic acid,** 4-hydroxy-, ethyl ester (Staudinger and Becker), A., i, 630.

2-**Ethoxyquinoline,** 6-nitro- (Kaufmann and de Petherd), A., i, 355.

5-**Ethoxytetramethyl-ψ-uric acid** (Biltz and Strufe), A., i, 300.

5-**Ethoxy-3:7:9-trimethyl-4:5-dihydrouric acid,** 4-hydroxy- (Biltz and Damm), A., i, 299.

5-**Ethoxy-ψ-uric acid** (Biltz and Heyn), A., i, 287.

Ethyl alcohol, heat of dilution of (MacInnes and Braham), A., ii, 560.
  heat of dilution of, in benzene (Gibbons), A., ii, 164.
  condensation of the vapour of (Andrén), A., ii, 192.

Ethyl alcohol, action of phosphoryl chloride on (Balareff), A., i, 625.
  reaction of sulphuric acid with (Evans and Albertson; Kremann), A., i, 314.
  oxidation of, by the liver (Hirsch), A., i, 67.
  effect of, on respiration and gaseous metabolism in man (Higgins), A., i, 489.
  estimation of (Villedieu and Hébert), A., ii, 155; (Ripper and Wohack), A., ii, 512.
  estimation of, in ethyl ether (Perkins), A., ii, 393.
  estimation of, in fermentation mixtures (Dox and Lamb), A., ii, 47.
  estimation of, in urine (Widmark), A., ii, 547.
  estimation of water in (Nussbaum), A., ii, 215.
Ethyl ether, viscosity of the system: antimony trichloride and (Kurnakov, Perlmutter, and Kanov), A., ii, 360.
  ferric chloride (Forster, Cooper, and Yarrow), T., 809; A., i, 646.
  estimation of alcohol and water in (Perkins), A., ii, 393.
Ethyl chloride, physical constants of (Berthoud), A., ii, 237.
  bromomalonyl chloride (Staudinger and Becker), A., i, 630.
Ethylamine, physical constants of (Berthoud), A., ii, 237.
Ethylamine, bromo-, preparation of (Gabriel), A., i, 541.
5-Ethylamino-ψ-uric acid (Biltz and Heyn), A., i, 287.
Ethyl*syn*benzhydroximic acid, rearrangement of, and its derivatives (Kuhara and Ishikawa), A., i, 87.
o-**Ethylbenzyl** bromide, and its derivatives (v. Braun), A., i, 259.
1-*o*-Ethylbenzylpiperidine, and its salts (v. Braun), A., i, 259.
6-α-Ethylbutyryl-4:7-dimethyl-2:2-diethylhydrindene-5-carboxylic acid (Freund, Fleischer, and Gofferjé), A., i, 574.
α-Ethylbutyrylurethane (Odaira), A., i, 81.
Ethylcarbamide, bromo- (Gabriel), A., i, 541.
4-Ethylcarbonatotoluene-3-sulphinic acid, and its methyl ester (Zincke and Arnold), A., i, 264.
4-Ethylcarbonatotoluene-3-sulphonic acid, derivatives of (Zincke and Arnold), A., i, 263.
4-Ethylcarbonatotolyl 3-*di*sulphide (Zincke and Arnold), A., i, 263.
Ethylcarbonatovanillin (Lapworth and Wykes), T., 792.
β-**Ethylcinnamic acids**, stereoisomeric, and their derivatives (Stoermer, Grimm, and Laage), A., i, 648.
Ethylene, compounds of aluminium chloride and (Gangloff and Henderson), A., i, 533.
  action of bromine water on (Read and Williams), T., 240; A., i, 313.
  *di*bromide, condensation of dimethylaniline and (v. Braun and Arkuszewski), A., i, 175.
  oxides (Bodforss), A., i, 223.
Ethylene, *tetra*chloro-, ultra-violet absorption spectra of (Massol and Faucon), A., ii, 188.
Ethylene glycol, preparation of (Brooks and Humphrey), A., i, 533.
Ethylenedioxybenzene, 4:5-*di*nitro-6-amino-, and 4:5:6-*tri*nitro- (G. M. and R. Robinson), T., 935.
2:3-Ethylenedioxyphenanthraphenazine (G. M. and R. Robinson), T., 935.
β-**Ethyl galactoside**, preparation of, from fruit kernels (Mougne), A., i, 379.
ε-**Ethylheptan-δ-one-γε-dicarboxylic acid**, ethyl ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 147.
3-Ethylhydrindone, 2:3:6(?)-*tri*bromo- (Stoermer and Laage), A., i, 654.
Ethylideneazobenzene-*p*-hydrazone, chloro-, sulphate (Tröger and Piotrowski), A., i, 668.
3-Ethylindone, and its semicarbazone and 2:6(?)-*di*bromo- (Stoermer and Laage), A., i, 654.
1-Ethylnaphthalene, 4-hydroxy-1-β-amino-. See 4-Ethyl-α-naphthol, 4-β-amino-.
4-Ethyl-α-naphthol, 4-β-amino-, and its derivatives (Windaus and Bernthsen-Buchner), A., i, 690.
Ethyl*cyclo*propane, preparation and transformations of (Rozanov), A., i, 84.
Ethylpropylacetophenoneoxime (Dumesnil), A., i, 654.
3-Ethylrhodanine-5-acetamide (Kallenberg), A., i, 280.
β-**Ethyl*di*thiocarbamylsuccinamic acids** (Kallenberg), A., i, 279.
Ethyl-*o*-toluidine, 3:4:5-*tri*nitro- (Jansen), A., i, 129.
Ethyluric acids (Biilmann and Bjerrum), A., i, 588.
α-**Ethylvalerylcarbamide**, α-bromo- (Odaira), A., i, 81.
α-**Ethylvalerylurethane** (Odaira), A., i, 81.

Ethylzingerone (NOMURA), T., 773; A., i, 570.

Eucommia ulmoides, caoutchouc from (SIEVERS), A., i, 346.

Eugenyl p-nitrobenzyl ether (REID), A., i, 333.

Euglobulin, conversion of ψ-globulin into (BERG), A., i, 485.

Euxenite from Ontario (MILLER and KNIGHT), A., ii, 538.

Evaporation apparatus (PLAISANCE and PERVIER), A., ii, 378.

Exosmosis (BROOKS), A., i, 371.

Explosives, lecture experiments on the theory of (EGGERT and SCHIMANK), A., ii, 462.
- nitrated, mixtures of (GIUA), A., i, 19.
- microchemical analysis of (ALMSTRÖM), A., i, 541.
- analysis of substances used in, by means of "nitron" (COPE and BARAB), A., ii, 268.

Extraction apparatus, Soxhlet (TWISS and MCCOWAN), A., ii, 418.

F.

Fæces, excretion of calcium in, and its hydrion concentration (NELSON and WILLIAMS), A., i, 103.
- detection of blood in (THEVENON and ROLLAND), A., ii, 432.
- estimation of fatty acids and soaps in (SHARPE), A., ii, 516.

Fats, saponification of (TREUB), A., ii, 528.
- hydrolysis of, by lipase (TANCOV), A., i, 182.
- fractionation of (SEIDENBERG), A., i, 626.
- formation of cholesterol esters in degeneration of (VALENTIN), A., i, 715.
- metabolism of. See Metabolism.
- estimation of unsaponifiable matter in (DAVIDSOHN), A., ii, 183; (WILKIE), A., ii, 429.
- separation of cholesterol and phytosterol from (PRESCHER), A., ii, 275, 514.

α-**Fenchene**, synthesis of (KOMPPA and ROSCHIER), A., i, 466.

Fenchenes, nomenclature of (KOMPPA and ROSCHIER), A., i, 398.

Fenchone, use of, in cryoscopic measurements (JONA), A., ii, 524.

Fenchylene, and its nitrosochloride (NAMETKIN and RUSHENCEVA), A., i, 152.

*iso***Fenchylxanthic acid**, methyl ester (NAMETKIN and RUSHENCEVA), A., i, 152.

Fermentation (BIEDERMANN), A., i, 62.
- equilibrium in (LICHTWITZ), A., i, 681.
- effect of slight increases of temperature on (RICHET and CARDOT), A., i, 107.
- activators of (V. EULER and HAMMARSTEN), A., i, 71.
- of dibasic acids (LEBEDEV), A., i, 188.
- action of toluene on (BUCHNER and SKRAUP), A., i, 613.
- alcoholic (LINDET), A., i, 188; (HARDEN), A., i, 501; (NEUBERG and FÄRBER), A., i, 502; (WILENKO; V. EULER and HALDIN), A., i, 680.
- citric acid, by *Aspergillus niger* (CURRIE), A., i, 614.
- lactic, effect of thallium salts on (RICHET), A., i, 370.

Ferments. See Enzymes.

Ferric salts. See under Iron.

Ferricyanides, estimation of, volumetrically (DE COQUET), A., ii, 551.

Ferrification in soils (BROWN and CORSON), A., i, 248.

Ferrochrome, estimation of chromium in (HERWIG), A., ii, 104; (KOCH), A., ii, 337, 392; (SCHUMACHER), A., ii, 337.

Ferrocyanides, crystal form and isomerism of (BENNETT), T., 490; A., i, 449.

Ferro-ferricyanide electrode. See Electrode.

Ferrum hydrogenio reductum, analysis of (WINKLER), A., ii, 511.

Fertilisers. See Manures, artificial.

Fibres, use of, in microscopic qualitative chemical analysis (CHAMOT and COLE), A., ii, 576.
- vegetable, purification of (STADNIKOV), A., i, 119.

Fibrin (HEKMA), A., i, 101; ii, 22, 23; (HOWELL), A., i, 101; (DIESSELHORST and FREUNDLICH), A., i, 180.
- analyses of (GORTNER and WUERTZ), A., i, 711.

Fibrinogen, effect of keeping solutions of (NOLF), A., i, 420.

Ficus javanica, orange-yellow in leaves of (MOLISCH), A., i, 506.

Filters, soluble (WILKIE and ANDERSON), A., ii, 224.

Filter flask (SHAW), A., ii, 499.

Filter paper, extraction of reducing substances from (MCBRIDE and SCHERRER), A., ii, 326.

Filtration, excluding air and moisture during (REDDELIEN), A. ii, 461.

Filtration apparatus (WEGELIN), A., ii, 462; (BOERICKE), A., ii, 547.

Fir, Douglas, constituents of the oleoresin of (Schorger), A., i, 467.

Firefly, bioluminescence in (Harvey), A., i, 365.

Fish, fresh-water, non-protein nitrogen in blood of (Wilson and Adolph), A., i, 360.

Fish-liver oil, new hydrocarbon from (Chapman), T., 56; A., i, 193.

Flame, propagation of, the uniform movement in (Mason and Wheeler), T., 1044.
  in mixtures of acetone and air (Wheeler and Whitaker), T., 267; A., ii, 249.
  in mixtures of acetylene and air (Haward and Sastry), T., 841; A., ii, 527.

Flames, Bunsen, chemical reactions in, under diminished pressure (Ubbelohde and Anwandter), A., ii, 569.
  highly luminous coloured, production of (Hemsalech), A., ii, 523.

Flame arc, use of, in chemical manufacture (Mott and Bedford), A., ii, 6.

Flavine (Browning, Gulbransen, Kennaway, and Thornton), A., i, 240.

Flavones, detection and physiological significance of, in plants (Shibata, Nagai, and Kishida), A., i, 107.

Flour, analysis of (Swanson and Tague), A., ii, 276.

Fluidity (Drucker), A., ii, 409.

Fluoran, *tetra*chloro-, amino- and nitro-derivatives of (Orndorff and Kennedy), A., i, 347.

Fluorene-9-acetic acid, and its ethyl ester (Wislicenus and Eble), A., i, 272.

α-Fluorenedimethylhydrindene. See α-*o*-Benzylene-2:2-dimethylhydrindene.

α-Fluorenedimethylindandione. See (α)-1:3-Diketo-*o*-benzylene-2:2-dimethylhydrindene.

Fluorenonedimethylindandiones. See 1:3-Diketo-*o*-benzoylene-2:2-dimethylhydrindenes.

Fluorenyl *iso*propyl ketone. See *iso*-Butyrylfluorene.

Fluorine, preparation of (Ruff), A., ii, 201; (Brauner), A., ii, 202.
  Hydrofluoric acid, separation of hydrofluosilicic acid and (Dinwiddie), A., ii, 39.
  Hydrofluosilicic acid, separation of hydrofluoric acid and (Dinwiddie), A., ii, 39.

Fluorine, estimation of (Dinwiddie), A., ii, 99.

Foods, physical chemistry of (Paul), A., i, 246, 507, 509.
  effect of high temperature on the nutritive value of (Hogan), A., i, 492.
  containing sugar, analysis of (Lajoux and Ronnet), A., ii, 582.
  detection and estimation of "saccharin" in (Bonis), A., ii, 430.
  estimation of alkalinity of the ash of (Kolthoff), A., ii, 386.
  estimation of chlorine in (Weitzel), A., ii, 501.
  estimation of iodine in (Bohn), A., i, 192.
  estimation of oxalic acid in (Arbenz), A., ii, 583.
  estimation of salicylic acid in (Steenbergen), A., ii, 549.

Formaldehyde, condensations of (Woker and Maggi), A., i, 686.
  condensation of amines with (Kroneberg), A., i, 170.
  action of ammonium chloride with (Werner), T., 844; A., i, 632.
  condensation of ammonium thiocyanate with (Schmerda), A., i, 545.
  condensation of cholic acid and (Synthetic Patents Co.), A., i, 318.
  condensation of pyrrole and its derivatives with (Tschelincev and Maksorov), A., i, 164.
  semicarbazone (Hess, Eichel, and Uibrig), A., i, 352.
  action of, on starch (Woker), A., i, 61, 447; (v. Kaufmann), A., i, 251; (Maggi and Woker), A., i, 686.
  action of, on sugars (Heiduschka and Zirkel), A., i, 446.
  detection of, in plants (Curtius and Franzen), A., i, 435.
  use of, in micro-titration (Clementi), A., ii, 400.
  titration of substituted amino-acids with (Clementi), A., ii, 344.

Formalin, estimation of (Stutterheim), A., ii, 430.

"Formazyl methylenecamphor" (Rupe and Burckhardt), A., i, 142.

Formic acid, electrolytic decomposition of, with rhodium electrodes (Wladislaw), A., ii, 136.
  kinetics of oxidation of, and its salts (Dhar), T., 707; A., ii, 458.
  catalytic reduction with (Mailhe and de Godon), A., i, 315.
  salts of, decomposition of (Gianoli), A., ii, 85.
  aluminium salt, astringent action of (Loewy and Wolffenstein), A., i, 497.

Formic acid, esters, viscosity of the systems stannic chloride and (Kurnakov, Perlmutter, and Kanov), A., ii, 360.
  methoxymethyl ester (Clark, Cox, and Mack), A., i, 316.
  p-nitrobenzyl ester (Reid), A., i, 333.
  detection and estimation of, in meat extract (Waser), A., ii, 343.
Formyl-*p*-aminobenzeneazo-β-naphthol (Morgan and Upton), T., 193.
Formylnaphthylacetic acids, ethyl esters (Wislicenus and Elvert), A., i, 202.
Formylphenylacetic acid, methyl ester, isomerism and derivatives of (Wislicenus, Börner, Kurtz, and Bilhuber), A., i, 268.
Formyl-*p*-phenylenediazoimide (Morgan and Upton), T., 190; A., i, 300.
Forsterite, equilibrium of anorthite, silica and (Boeke), A., ii, 147.
Frangula, detection of (Beal and Okey), A., ii, 279.
Freezing point, apparatus for determining lowering of (van Name and Brown), A., ii, 163.
  lowering of, in solutions of metallic salts and their mixtures (Hall and Harkins), A., ii, 65; (Harkins and Roberts), A., ii, 66.
Friedel-Crafts' reaction (Copisarow), T., 10; A., i, 144; (Boedtker and Halse), A., i, 124.
d-**Fructose**. See Laevulose.
Fruits, preparation of extract of (Thoms), A., i, 721.
Fuchsone, additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 209.
Fucic acid (Odén), A., i, 379.
Fucose, oximes and hydrazones of, and their derivatives (Votoček), A., i, 250.
Fucose-*p*-tolylhydrazone (van der Haar), A., i, 380.
Fucus virsoides, constituents of (Votoček and Röhlich), A., i, 438.
Fulminic acid, salts of (Wöhler and Martin), A., i, 383.
Fumaric acid, compound of aluminium chloride and (Gangloff and Henderson), A., i, 533.
  p-nitrobenzyl ester (Lyman and Reid), A., i, 334.
Fumaric acid, chloro-, *p*-nitrobenzyl ester (Lyons and Reid), A., i, 559.
Fumaryldiglycinamide (Bornwater), A., i, 121.
Furfuraldehyde, kinetics of formation of, from arabinose (Kremann and Klein), A., ii, 251.
Furfuraldehyde, compounds of aluminium and ferric chlorides and (Gangloff and Henderson), A., i, 533.
  action of cinnamylidenemethyl methyl ketone with (Giua), A., i, 408.
  estimation of (Dox and Plaisance), A., ii, 53.
Furfuroids of barley, enzymic hydrolysis of (Baker and Hulton), T., 121; A., i, 310.
Furfurylideneazobenzene-*p*-hydrazone salts (Tröger and Piotrowski), A., i, 669.
Furoxans. See *iso*Oxadiazole oxides.
Fuscazinic acid (Staněk), A., i, 382.

G.

Gadolinite from the Radauthal, Harz (Fromme), A., ii, 497.
Galactobioses, synthesis and crystallisation of (Bourquelot and Aubry), A., i, 250.
Galactose, rotatory power of, in propyl alcohol (Foulkes), A., i, 79.
  action of alkalis on (Waterman), A., i, 631.
d-**Galactose**, detection of, by means of its *o*-tolylhydrazone (van der Haar), A., ii, 515.
Galactosegalacturonic acid (Ehrlich), A., i, 322.
d-**Galactose-*p*-tolylhydrazone** (van der Haar), A., i, 380.
β-**Galactosidase** in plants (Mougne), A., i, 438.
Galena ores, occurrence of silver in (Nissen and Hoyt), A., ii, 144.
Gallium, electrolytic deposition and purification of (Uhler and Browning), A., ii, 34.
  detection and separation of (Browning and Porter), A., ii, 544.
Gallonitrile, and its triacetyl derivative (Fischer and Nouri), A., i, 393.
Gall stones, human (Salkowski), A., i, 716.
Gas, detonating, ignition point of (Mitscherlich), A., ii, 199.
  illuminating, experiment to show the enrichment of (Baker), A., ii, 255.
    action of, on plants (Wehmer), A., i, 507.
Gas absorption apparatus (Richmond and Hembrough), A., ii, 215.
Gas analysis (Descamps), A., ii, 216; (Brandt), A., ii, 384; (Henderson and Morriss), A., ii, 506.
  reagents for use in (Anderson), A., ii, 39.

Gas analysis apparatus (Hauser), A., ii, 266, 338; (Gregg), A., ii, 379; (Hamburger and Koopman), A., ii, 500.

Gas-collecting apparatus (Wempe), A., ii, 529.

Gas generator (Fernandez), A., ii, 255.

Gas meter, laboratory (Beckett), A., ii, 137.

Gas volumeter (Deming), A., ii, 576.

Gas-washing apparatus (Gray), T., 179; A., ii, 198.

Gases, diatomic, infra-red absorption spectra of (Brinsmade and Kemble), A., ii, 402.
electric discharge through (Wright), T., 643; A., ii, 403.
compressed, disruptive discharge in (Guye and Stanescu), A., ii, 231.
ionisation of (Wellisch), A., ii, 352.
specific heat of, variation of, with pressure (Lussana), A., ii, 120.
ideal, additivity of internal atomic heats in (Trautz), A., ii, 439.
density of (Schmidt), A., ii, 406; (Edwards), A., ii, 442.
correction of volumes of (Rigotard), A., ii, 179.
apparatus for (Fenby), A., ii, 379.
viscosity of (Drucker), A., ii, 409.
liquefied, viscosity of (Verschaffelt; Verschaffelt and Nicaise), A., ii, 408.
compound, velocity of dissociation of (March), A., ii, 196.
diffusion of, apparatus for (Marcus), A., ii, 409.
of equal molecular weight, separation of, by thermal diffusion (Chapman), A., ii, 444.
equilibrium and reaction velocity in (Trautz), A., ii, 23.
inflammability of mixtures of (Thornton), A., ii, 172.
electrical ignition of (Wheeler and Greenwell), T., 130; A., ii, 171.
ignition of mixtures of (McDavid), T., 1003; (Mason and Wheeler), T., 1044.
laboratory apparatus for evolution of (Angeli), A., ii, 173.

Gasolene vapour, estimation of, in air (Anderson), A., ii, 338.

Gastric juice, analysis of, by electrometric titration (Michaelis), A., ii, 228.
estimation of acidity of (Fowler, Bergeim, and Hawk), A., ii, 49.

Gehlenite, constitution of (Clarke), A., ii 417.

Gelatin, osmotic pressure of (Biltz, Bugge, and Mehler), A., ii, 17.
absorption of water by (Ostwald), A., i, 99.

α- and β-**Gelatins**, optical activity of (Rakuzin and Braudo), A., i, 181.

Gelatinates, alkali, optical activity of (Rakuzin and Braudo), A., i, 181.

Gels, theory of the structure of (Hatschek), A., ii, 451.
vapour pressure of (Bachmann), A., ii, 562.
adsorption in (Bradford), A., ii, 366.

Generator gas, analysis of (Kropf), A., ii, 541.

Geneserine, constitution of (Polonovski), A., i, 706.

Genital glands. See Glands.

Gentiobiose, derivatives of, and their rotatory powers (Hudson and Johnson), A., i, 446.

Germanium, occurrence of, in zinc ores (Buchanan), A., ii, 416.
detection of, and its separation from arsenic (Browning and Scott), A., ii, 546.

Ginger, pungent principles of (Nomura), T., 769; A., i, 570; (Lapworth, Pearson, and Royle), T., 777; A., i, 571; (Lapworth and Wykes), T., 790; A., i, 572; (Nelson), A., i, 572.

Gingerol (Nelson), A., i, 572.
preparation and properties of, and its derivatives (Lapworth, Pearson, and Royle), T., 777; A., i, 571.

Glands, ductless, phosphatides in (Fenger), A., i, 67.
genital, influence of extract of, on phosphorus metabolism (Jean), A., i, 304.

Glands. See also Pituitary and Thyroid.

Glass, estimation of boric acid in (Nicolardot and Boudet), A., ii, 383.

Glass sand, estimation of iron in (Ferguson), A., ii, 581.

Glauconite (Hart), A., ii, 537.

Globulin, estimation of, colorimetrically (Autenrieth), A., ii, 400.

ψ-**Globulin**, transformation of, into englobulin (Berg), A., i, 485.

Glomerella cingulata, utilisation of pentoses and their compounds by (Hawkins), A., i, 503.

Glucinum, melting point and heat of fusion of (Oesterheld), A., ii, 89.

Glucinum alloys with aluminium, with copper, with silver, and with iron (Oesterheld), A., ii, 89.

Glucinum vanadates (Brinton), A., ii, 32.

Gluconic acid, hydrazides of (Weerman), A., i, 548.

Glucose, commercial, composition of, and its digestibility (Wesener and Teller), A., i, 7.
d-**Glucose**. See Dextrose.
β-**Glucose**, preparation of (Mangam and Acree), A., i, 446.
β-**Glucosidase**, influence of acetic acid on properties of (Bourquelot and Aubry), A., i, 99.
Glucosides, synthesis of (Fischer and v. Mechel), A., i, 216; (Fischer and Bergmann), A., i, 467.
  digitalis (Kiliani), A., i, 468.
Glucosides. See also:—
  Ampelopsin.
  Amygdalin.
  Asterin.
  Callistephin.
  Chrysanthemin.
  Keracyanin.
  Pelargonenin.
  Petunin.
  Prunicyanin.
  Salvianin.
  Salvinin.
  Sambunigrin.
  Violanin.
Glutamic acid, crystallography of salts of (Kaplanova), A., i, 547.
  electrolytic diazotisation of (Krauss), A., i, 548.
  separation of, from amino-acids (Corti), A., i, 634.
Glutose (Pellet), A., ii, 223.
Glyceraldehyde, sterical relationship of tartaric acid and (Wohl and Momber), A., i, 319.
Glycerol, ninhydrin reaction with (Harding), A., ii, 274.
  β-glucoside, crystallisation and properties of (Bourquelot, Bridel, and Aubry), A., i, 379.
  estimation of (Kipper and Wohack), A., ii, 512; (Löfel), A., ii, 547.
Glycerophosphoric acid, constitution of esters of (Bailly), A., i, 2.
s-**Glycine**-*p*-**methoxyphenylalaninocarbamide**, and its dipotassium salt (Johnson and Hahn), A., i, 476.
p-**Glycinephenoxyacetic acid**, and its derivatives (Jacobs and Heidelberger), A., i, 696.
Glycogen in the liver (McDanell and Underhill), A., i, 364.
  effect of soaps on the diastatic fermentation of (Kende), A., i, 615.
Glycollic acid, preparation of (Witzemann), A., i, 316.
Glycols, preparation of (Gulf Refining Co.), A., i, 377.
α-**Glycols**, transformation of (Coma y Roca), A., i, 266.
Glycolysis (Wilenko; v. Euler and Haldin), A., i, 680.
Glycosuria. See Diabetes.
Glycuronic acid, isomeride of (Suarez), A., i, 249.
  benzeneazo-phenol and -resorcinol esters (Salant and Bengis), A., i, 70.
Glycylglycine, rate of hydrolysis of, by ereptase (Dernby), A., ii, 82.
Glycyrrhizin, estimation of, in liquorice (Linz), A., ii, 430.
Glyoxal, depolymerisation of (Hess and Uibrig), A., i, 319.
Glyoxylic acid, and its esters, isomeric hydrazones and semicarbazones of (Busch, Achterfeld, and Seuffert), A., i, 228.
Gob fires in coal mines, formation of hydrogen sulphide by (Drakeley), T., 853; A., ii, 530.
Gold, high-frequency spectrum of (Ledoux-Lebard and Dauvillier), A., ii, 283.
  volatility of (Mostowitsch and Pletneff), A., ii, 213.
  colloidal (Gutbier and Wagner), A., ii, 169.
    preparation of solutions of (Reitstötter), A., ii, 481.
    coagulation of solutions of (Zsigmondy), A., ii, 366.
    action of mercuric chloride on solutions of (Herstad), A., ii, 168.
Gold alloys with manganese (Hahn and Kyropoulos), A., ii, 476.
Gossypol and its dianiline salt (Carruth), A., i, 719.
Goyazite, identity of hamlinite with (Schaller), A., ii, 177.
Grapes, anthocyanins of (Willstätter and Zollinger), A., i, 47.
  green, brown colour on (Molisch), A., i, 506.
Graphite, structure of (Debye and Scherrer), A., ii, 437.
Greensand (Hart), A., ii, 537.
Griffithite from California (Larsen and Steiger), A., ii, 148.
Grignard reagents, action of, on cyanamides (Adams and Beebe), A., i, 96.
Growth (Robertson), A., i, 65; (Robertson and Delprat), A., i, 673.
  effect of diet on, in rats (Osborne and Mendel), A., i, 238.
Guaiacol, bromo- and bromonitro-derivatives (Hindmarsh, Knight, and Robinson), T., 940; A., i, 693.
  6-bromo-4 and -5-nitro- (Jones and Robinson), T., 917.
  4-chloro-5-nitro- (Gibson, Simonsen, and Rau), T., 82; A., i, 204.

- **Guaiacolsulphonic acid,** *di*bromo- and *di*iodo-, salts of (Krauss and Crede), A., i, 557.
- **Guanidine,** preparation of (Sharpe), A., i, 121.
  - formation of, from cyanamide and from thiocarbamide (Schmidt), A., i, 449.
- **Guanidinium** palladochloride (Gutbier, Fellner, Kräutter, Falco, Krell, Schulz, and Woernle), A., i, 541.
  - palladotrichloride and amino- (Gutbier and Fellner), A., i, 542.
- **Guanine-nucleotide,** preparation and structure of, and its brucine salt (Read), A., i, 596; (Jones and Read), A., i, 597.
- **Guanylic acid.** See Guanine-nucleotide.
- **Guinea-pigs,** metabolism of (Smith and Lewis), A., i, 714.
- **Guldberg's rule,** application of, to homologous series (Herz), A., ii, 441.
- **Gypsum,** use of, as a fertiliser (Nolte), A., i, 624.

H.

- **Hæmatic acid,** synthesis of (Küster and Weller), A., i, 443.
- **Hæmatin,** oxidation of (Küster and Weller), A., i, 443.
- **Hæmatoporphyria congenita** (Schumm), A., i, 715.
- **Hæmochromogen,** acid, preparation of (Dhéré), A., i, 519.
  - crystallisation of (Dhéré, Baudoux, and Schneider), A., i, 712.
- **Hæmocyanin** (Dhéré), A., i, 236.
- **Hæmoglobin,** colourless crystals of (Harris), A., i, 64.
- **Halloysite** from Colorado (Larsen and Wherry), A., ii, 265.
  - so-called, from Georgia and Alabama (van der Meulen), A., ii, 177.
- **Halogens,** atomic volumes of, at the critical point (Le Bas), A., ii, 193.
  - estimation of, electrolytically (Aten), A., ii, 419.
  - estimation of, in organic compounds (Kelber), A., ii, 215; (Lemp and Broderson), A., ii, 539.
- **Halogen acids,** absorption of light by (Brannigan and Macbeth), A., ii, 2.
  - action of light on the formation and decomposition of (Coehn and Stuckardt), A., ii, 5.
- **Halogen ions,** electrolysis of solutions containing (Aten), A., ii, 190.
- **Hamlinite,** identity of goyazite with (Schaller), A., ii, 177.
- **Heat,** capacity for, and free energy (Bell; Richards), A., ii, 65.
    - and entropy (Njegovan), A., ii, 405.
  - internal atomic, additivity of, in ideal gases (Trautz), A., i, 439.
  - specific, of cadmium standard cells (Seibert, Hulett, and Taylor), A., ii, 231.
    - of elements (Mills), A., ii, 356.
    - of gases, variation of, with pressure (Lussana), A., ii, 120.
    - of solutions (Kolosovski), A., ii, 65.
- **Heat of combustion** of organic compounds (Thornton), A., ii, 164.
- **Heat of dilution,** measurement of (MacInnes and Braham), A., ii, 560.
- **Heat of solution** in mixed solvents (Kolosovski), A., ii, 67.
- **Heat of vaporisation** (Leduc), A., ii, 193.
- **Helianthin.** See Methyl orange.
- **Helicorubin** (Dhéré and Vegezzi), A., i, 421.
- **Helium,** spectrum of (Merton and Nicholson), A., ii, 433; (Merrill), A., ii, 434; (Richardson and Bazzoni), A., ii, 521.
  - ionisation potential of (Bazzoni), A., ii, 63.
- **Hemimellitic acid,** 1:3-dimethyl ester, sodium derivative (Meyer and Wesche), A., i, 341.
- *n*-**Heptaldehyde,** derivatives of (Harries and Oppenheim), A., i, 211.
- **Heptan-δ-one-γε-dicarboxanilic acid,** ethyl ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 147.
- **Heptinenearsine oxide,** chloro- (Synthetic Patents Co.), A., i, 196.
- **Heptinenearsinic acid,** chloro- (Synthetic Patents Co.), A., i, 196.
- *n*-**Heptoylurethane** (Odaira), A., i, 81.
- **Heterocodeine** and its methochloride (Mannich), A., i, 474.
- **Heteropoly-acids** (Rosenheim, Pieck, and Pinsker), A., ii, 35; (Rosenheim and Pieck), A., ii, 212.
- **Hexaethylbenztrihydrindene-1:3-dione.** See 1:3-Diketohexaethyltritrimethyleneбenzene.
- **Hexahydrocomenic acid,** and its lactone (Borsche), A., i, 118.
- **Hexahydropyrimidine,** hydrolysis of (Branch), A., ii, 24.
- **Hexamethylbenzene,** additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 207.
- **Hexamethylene** sulphide, and its derivatives (Grischkevitsch-Trochimovski), A., i, 157.

Hexamethylenetetramine (*hexamethyleneamine; urotropine*), compounds of, with metallic salts (VIVARIO and WAGENAAR), A., ii, 179.
  explosive peroxide derivative of (LEULIER), A., i, 251.
  detection of (CARLES), A., ii, 159.
  estimation of (SUGIURA and FALK), A., ii, 54.
Hexamethylenetetraminemethylhydroxide, preparation of salts of (SCHMITZ), A., i, 324.
Hexamethylstilbene, additive compounds of (PFEIFFER, JOWLEFF, FISCHER, MONTI, and MULLY), A., i, 207.
Hexane, equilibrium of mixtures of aniline and (KEYES and HILDEBRAND), A., ii, 565.
Hexanes, thermal and pressure decomposition of (EGLOFF), A., i, 109.
*cyclo***Hexanol** and its homologues, isomeric transformations in (ROZANOV), A., i, 132.
  condensation of *sec.*-butyl alcohol with (GUERBET), A., i, 694.
*cyclo***Hexanone**, condensation of pyrrole with (TSCHELINCEV, TRONOV, and KARMANOV), A., i, 412.
Hexoic acid, distillation of, in steam (RICHMOND), A., i, 316.
n-**Hexoic acid**, *α*-amino-, *p*-nitrobenzyl ester (LYONS and REID), A., i, 559.
*iso***Hexoylglycinic acid**, *α*-bromo-, ethyl ester (BORNWATER), A., i, 121.
*cyclo***Hexylacetone**. See *cyclo*Hexylmethyl methyl ketone.
α-*cyclo***Hexylbutan-*β*-ol**, and its salts (GUERBET), A., i, 694.
*cyclo***Hexylcarbinol** and its derivatives, isomeric transformations in (ROZANOV), A., i, 132.
*cyclo***Hexylmethyl ethyl ketone**, and its semicarbazone (GUERBET), A., i, 694.
*cyclo***Hexylmethyl methyl ketone**, and its derivatives (GUERBET), A., i, 453.
γ-*cyclo***Hexyl*iso*propyl alcohol**, and its derivatives (GUERBET), A., i, 453.
Hide powder, preparation of (ZALKIND and EGORKIN), A., ii, 160.
  adsorption of chromic oxide by (DAVISON), A., ii, 241.
Hippenylcarbamidoacetic acid, ethyl ester, and its derivatives (CURTIUS and LAURENT), A., i, 200.
Hippenylcarbamidosuccinic acid, and *p*-bromo-, and their salts and derivatives (CURTIUS and ZIMMERLI), A., i, 200.
Hippenylcarbamidosuccinimide, *N*-amino- (CURTIUS and ZIMMERLI), A., i, 200.
Hippenylcarbamidosuccinyldiazide (CURTIUS and ZIMMERLI), A., i, 200.
Hippuric acid, *p*-nitrobenzyl ester (LYMAN and REID), A., i, 334.
  estimation of, in animal tissues and fluids (ITO), A., ii, 52.
Hippuric acids, *o*- and *p*-nitro-, esters and azides of (CURTIUS and PETRIDIS), A., i, 202.
Histidine, conversion of, into urocanic acid by bacteria (RAISTRICK), A., i, 499.
Högbomite (GAVELIN), A., ii, 324.
Hofmann reaction (v. BRAUN), A., i, 169.
Hollandus, Jan Isaac and Isaac, the alchemists (JORISSEN), A., ii, 198, 529; (HOLGEN), A., ii, 461; (SCHELENZ), A., ii, 529.
Homoeriodictyol, constitution of (OESTERLE and KUENY), A., i, 703.
Homoveratrole, 6-bromo-, and 6-bromo-5-nitro- (JONES and ROBINSON), T., 919.
Homoveratrole-6-sulphonamide (BROWN and ROBINSON), T., 955.
Honey, biological examination of (GADAMER and LASKE), A., ii, 395.
  analysis of (ATKINS), A., ii, 157.
Hordeum vulgare, seeds of. See Seeds.
Hornblende (DI FRANCO), A., ii, 498.
Humin substances, synthesis of (MAILLARD), A., i, 251.
Humus (GORTNER), A., i, 310, 311.
  formation of, by plants (TROUSSOV), A., i, 189.
Humus-phosphoric acid (GORTNER and SHAW), A., i, 376.
spiro-**5:5-Hydantoin** (BILTZ and HEYN), A., i, 288.
Hydantoins (FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING; JOHNSON and HAHN), A., i, 475.
*spiro***Hydantoins** (BILTZ, HEYN, and BERGIUS), A., i, 290.
Hydantoin-5-carboxyamide, 5-hydroxy- (BILTZ and HEYN), A., i, 289.
Hydantoin-2-indolindigo, *iso*thio-. See 4-Keto-5-*ψ*-indoxylidenethiazolidine, 2-imino-.
Hydnocarpus alcalæ, seeds of. See Seeds.
Hydramines of the piperidine and pyrrolidine series, action of aldehydes on (HESS, UIBRIG, and EICHEL), A., i, 351, 352.
Hydrargyrum thymolo-aceticum, constitution of (RUPP), A., i, 670.
Hydrates, crystalline, dehydration of (RAE), A., ii, 24.
Hydrazine, oxidation of (SOMMER), A., ii, 30.

Hydrazines, action of, with *p*-nitrosoamines (Fischer and Chur), A., i, 708.

Hydrazines, amino- (Franzen and v. Fürst), A., i, 58, 59.

2-Hydrazino-1-benzsulphonazole, and its derivatives (Schrader), A., i, 709.

β-**Hydrazinopropionic hydrazide**, and its dibenzylidene derivative (Curtius and Aufhäuser), A., i, 637.

2:2′-Hydrazobenzoic acid, 6:6′-*di*chloro-, ethyl ester (Reich and Merki), A., i, 228.

α-**Hydrindone**, 5- and 7-hydroxy- (v. Auwers and Hilliger), A., i, 38.

1-Hydrindylacetic acid, and its derivatives (v. Braun, Danziger, and Koehler), A., i, 260.

β-**1-Hydrindylethyl alcohol**, and its chloride (v. Braun, Danziger, and Koehler), A., i, 260.

1-Hydrindylideneacetic acid, ethyl ester (v. Braun, Danziger, and Koehler), A., i, 260.

1- and 2-Hydrindylmethylamines, and their salts and derivatives (v. Braun, Danziger, and Koehler), A., i, 260.

Hydriodic acid. See under Iodine.

Hydroaromatic compounds, behaviour of, in the animal organism (Sasaki), A., i, 677.

Hydrobromic acid. See under Bromine.

Hydrocarbon, $C_{20}H_{36}$, from polymerisation of *α*-phenyl-$\Delta^{\alpha\gamma}$-butadiene (Lebedev and Ivanov), A., i, 127.

Hydrocarbons, spectra of (Raffety), A., ii, 61.
  melting points of (Enklaar), A., i, 113.
  bromination of (Datta and Chatterjee), A., i, 15.
  iodination of (Datta and Chatterjee), A., i, 327.
  pyrogenesis of (Lomax, Dunstan, and Thole), A., i, 109.
  aliphatic chlorinated, viscosity of (Herz), A., ii, 194.
  aromatic, preparation of, from petroleum (Rittmann), A., i, 14; (Egloff and Twomey), A., i, 110.
    formation of, from thermal decomposition of natural gas condensates (Zanetti and Egloff), A., i, 450.
    amino-derivatives, additive compounds of *s*-trinitrobenzene with (Cadre and Sudborough), A., i, 85.
    higher, preparation of lower hydrocarbons from (Synthetic Hydrocarbon Co.), A., i, 15.
  unsaturated, refractometric indices of (Enklaar), A., i, 111.

Hydrochloric acid. See under Chlorine.

Hydrocinchoninone. See Cinchotinone.

Hydrocotarnine, action of cyanogen bromide on (v. Braun), A., i, 162.

Hydrocyanic acid. See under Cyanogen.

Hydrofluoric and **Hydrofluosilicic acids.** See under Fluorine.

Hydrogels, effect of freezing on (Foote and Saxton), A., ii, 241, 364.

Hydrogen, atomic weight of, and its volume combination with oxygen (Guye), A., ii, 412.
  distance between atoms in the molecule of (Silberstein), A., ii, 161.
  formation of, from formates, and from carbon monoxide and alkalis (Gianoli), A., ii, 85.
  apparatus for preparation of (Mosbacher), A., ii, 464.
  spectrum of (Stark), A., ii, 281; (Takamine and Yoshida), A., ii, 401; (Merton and Nicholson), A., ii, 433; (Richardson and Bazzoni), A., ii, 521.
  occlusion of, by a palladium cathode (Smith and Martin), A., ii, 64.
  liquid, viscosity of (Verschaffelt and Nicaise), A., ii, 408.
  union of oxygen and, in presence of catalysts (Hofmann and Ebert), A., ii, 25.
  reduction of sulphuric acid by (Jones), A., ii, 530.

Hydrogen bromide. See Hydrobromic acid under Bromine.
  chloride. See Hydrochloric acid under Chlorine.
  fluoride. See Hydrofluoric acid under Fluorine.
  iodide. See Hydriodic acid under Iodine.
  *per*oxide, formation of, from electrolysis of malonates (Schall), A., ii, 118.
    reaction of *p*-phenylenediamine with (Heiduschka and Goldstein), A., i, 482.
    use of, as a hydrolytic agent (McMaster and Langreck), A., i, 334.
    reactions of (Macri), A., ii, 529.
    estimation of (Jamieson), A., ii, 500.
    estimation of, volumetrically (Bury), A., ii, 216.
  sulphide, formation of, by gob fires in coal mines (Drakeley), T., 853; A., ii, 530.
    apparatus for generating (Bezzenberger), A., ii, 368; (Mossbacher), A., ii, 464.
    apparatus for precipitation with (Fuller), A., ii, 464.

Hydrogen sulphide, estimation of, iodometrically (Jayson and Oesper), A., ii, 577.
  estimation of, in water (Incze), A., ii, 502.
Hydrogen, estimation of, in organic compounds (Wise), A., ii, 541.
Hydrogen electrode. See Electrode.
Hydrogen ion, estimation of, in sea water (McClendon), A., ii, 266, 423.
Hydrohydrastinine, action of cyanogen bromide on (v. Braun), A., i, 162.
Hydroxy-acids, action of sodium hypochlorite on amides of (Weerman), A., i, 546.
  fatty, estimation of (Hodes), A., ii, 429.
Hydroxylamine hydrochloride, electrolytic preparation of (Schoch and Pritchett), A., ii, 29.
Hydroxylammonium chloroacetates (Jones and Werner), A., i, 380.
Hygrometers, use of cobalt salts in (Vanino), A., ii, 320.
Hyperglycæmia (McDanell and Underhill), A., i, 368.
  produced by injection of peptone (McGuigan and Ross), A., i, 528.
Hypochlorites. See under Chlorine.
Hypophosphoric acid. See under Phosphorus.
Hyposulphites. See under Sulphur.

I.

Ichthyol oils, constituents of (Scheibler), A., i, 153.
Ignition of gases (Wheeler and Greenwell), T., 130; A., ii, 171.
  of gaseous mixtures (McDavid), T., 1003; (Mason and Wheeler), T., 1041; (Thornton), A., ii, 172.
Ileum, hydrogen-ion concentration in the (McClendon, Shedlov, and Thomson), A., i, 602.
Ilsemannite (Schaller), A., ii, 491.
Imbibition, influence of electrolytes on (Ostwald), A., i, 99.
Imines, condensation of acetone with (Mayer), A., i, 144.
Iminodiacetic acid, amide of, and its β-naphthalenesulphonyl derivative (Bergell), A., i, 448.
Imino-esters (Knorr), A., i, 255, 547.
Iminothiocarbonic acid, ethoxyethyl ester (Dixon and Taylor), A., i, 12.
Immunity, theories of (Poyarkov), A., i, 427.
  adsorption in (Andreev), A., i, 183.
Indamines (Kehrmann and Poplawski), A., i, 416.
Indandione. See Diketohydrindene.
Indanthrene, preparation of chloro-derivatives of (Chemische Fabrik Griesheim Elektron; Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 479.
Indazinesulphonic acid (Kehrmann and Herzbaum), A., i, 592.
Indene series (Orechov), A., i, 127, 450; (v. Braun, Kruber, and Danziger), A., i, 130; (v. Braun, Danziger, and Koehler), A., i, 260; (Orechov and Grinberg), A., i, 450.
Indican, detection of, in urine (Askenstedt), A., ii, 553.
Indicators, theory of (Bjerrum), A., ii, 215.
  quinone-phenolate theory of (White and Acree), A., i, 340.
  colour change and degree of dispersity of (Kruyt and Kolthoff), A., ii, 452.
  relative value of, in titration of gastric juice (Fowler, Bergeim, and Hawk), A., ii, 49.
  use of sulphonephthaleins as (Lubs and Acree), A., ii, 97.
Indigotin, estimation of, volumetrically (Jones and Spaans), A., ii, 56.
Indigotin derivatives, absorption spectra and halochromism of (Lifschitz and Lourié), A., i, 586.
Indole, auto-oxidation of, in daylight (Baudisch and Hoschek), A., i, 166.
Indoles, condensation of aromatic aldehydes with (Hoschek), A., i, 167.
Indoxyl, detection of, in urine (Palet), A., ii, 553.
  detection and estimation of, in urine (Justin-Mueller), A., ii, 57.
Infants, feeding of (Bosworth and Bowditch), A., i, 184.
Inorganic compounds, structure of (Briggs), T., 253; A., ii, 254.
  absorption of light by (Brannigan and Macbeth), A., ii, 2.
  complex, cyclic theory of constitution of (Turner), A., ii, 28.
Inositol, utilisation of, in dogs (Greenwald and Weiss), A., i, 610.
Inositol phosphoric acid, and its strychnine salt (Rather), A., i, 315.
Insects, toxicity of benzene derivatives towards (Moore), A., i, 527, 678.
  diet required for nutrition of (Loeb and Northrop), A., i, 65.
Intestine, small, hydrogen-ion concentration in the (Long and Fenger), A., i, 492.
Intoxication (Jacoby), A., i, 71, 106; ii, 54.
Inulin, adsorption of (Rakuzin), A., ii, 294.

Inulin, diastatic degradation of, in chicory root (Wolff and Geslin), A., i, 720.
Invertase, kinetics of the action of (Nelson and Vosburgh), A., ii, 252.
effect of glycerol on the activity of (Bourquelot), A., i, 713.
Invert-sugar, action of acids on rotation of, in presence of soluble salts (Saillard and Wehrung), A., i, 513.
resorption of, in the body (Brahm), A., i, 428.
Iodates. See under Iodine.
Iodination (Datta and Chatterjee), A., i, 327; (Datta and Prosad), A., i, 332.
Iodine, atomic weight of (Guichard), A., ii, 201.
occurrence of, in marine algæ (Okuda and Eto), A., i, 437.
extraction and estimation of (van Os), A., ii, 267.
colloidal (Bordier and Roy), A., ii, 29.
action of alkalis on (Bougault), A., ii, 368.
velocity of solution of metallic cadmium in (van Name), A., ii, 411.
equilibrium of iodides with (van Name and Brown), A., ii, 455.
use of, in microchemistry (Sperlich), A., ii, 400.
Iodine compounds, action of ozone on (Riesenfeld and Bencker), A., ii, 201; (Harries), A., ii, 464.
Iodine:—
Hydriodic acid, photochemical oxidation of (Strachov), A., ii, 113.
Iodides, equilibrium of iodine with (van Name and Brown), A., ii, 455.
detection of, with palladium chloride, in presence of thiocyanates, ferrocyanides and ferricyanides (Curtman and Harris), A., ii, 267.
estimation of, in presence of bromides and chlorides (Kolthoff), A., ii, 420.
Iodates, velocity of reaction of sulphites with (Eggert), A., ii, 197.
Periodates, detection of, in presence of other per-salts (Monnier), A., ii, 98.
Iodine, estimation of, volumetrically, with thiosulphate (Kempf), A., ii, 502.
estimation of, in foods (Bohn), A., i, 192.
Iodometry, differential (Barnebey and Hawes; Barnebey), A., ii, 274; (Barnebey and Bishop), A., ii, 390.
Ions, discharge potentials of (Ghosh), A., ii, 352.
difference of potential due to adsorption of (Baur and Kronmann), A., ii, 231.
mobility of, in gases (Wellisch), A., ii, 352.
antagonistic action of (Feenstra), A., i, 70, 105.
hydration of (Newbery), T., 470; A., ii, 355.
tables for electromotive estimation of the concentration of (Matula), A., ii, 13.
Ionisation and adsorption (Reychler), A., ii, 233.
of acid salts in aqueous solution (Thoms and Sabalitschka), A., i, 700.
photoelectric, of solutions (Volmer), A., ii, 353.
positive, of heated metallic salts (Waterman), A., ii, 162.
Ionisation constants of unsaturated acids (Derick and Kamm), A., ii, 233.
Ionometer, direct reading (Bartell), A., ii, 235.
Ipecacuanha alkaloids (Pyman), T., 419; A., i, 410; (Keller; Karrer), A., i, 409.
pharmacology of (Walters and Koch), A., i, 612; (Walters, Eckler, and Koch), A., i, 717.
Iridium, high-frequency spectrum of (Ledoux-Lebard and Dauvillier), A., ii, 283.
colloidal, preparation of (Paal, Biehler, and Steyer), A., ii, 376.
chlorides and chloro-salts of (Delépine), A., ii, 537.
Iridotrioxalic acid, potassium salt, preparation of (Delépine), A., i, 627.
Iron, flame spectrum of (Hemsalech), A., ii, 61.
line spectrum of (Hemsalech), A., ii, 521.
passification of (Smits and de Bruyn), A., ii, 262.
corrosion of (Aston), A., ii, 191.
commercial sheet, corrosion of (E. A. and L. T. Richardson), A., ii, 175.
equilibrium of water vapour with (Wöhler and Prager), A., ii, 455.
carburation of, by alkali cyanides and cyanates (Portevin), A., ii, 476.
galvanised, stripping, analysis and testing of (Heise and Clemente), A., ii, 338; (Witt), A., ii, 337.

- **Iron alloys** with boron (Tschischevsky and Herdt), A., ii, 372.
  - with cerium (Vogel), A., ii, 259.
    - electrolytic deposition of (Kremann, Schadinger, and Kropsch), A., ii, 574.
  - with chromium and nickel, analysis of (Reid), A., ii, 392.
  - with copper (Ruer and Goerens), A., ii, 474.
  - with copper, nickel and tungsten (Irmann), A., ii, 478.
  - with glucinum (Oesterheld), A., ii, 89.
  - with nickel, expansion of (Guillaume), A., ii, 356.
- **Iron** oxides (Sosman), A., ii, 175.
  - sulphates, occurrence and genesis of (Scharizer), A., ii, 490.
  - ammonium alum, hydrolysis of (Rae), A., ii, 94.
  - sulphide, electrolytic analysis of (Williams), A., ii, 425.
  - *di-* and *tri-*sulphides (Rodt), A., ii, 142.
  - **Ferric** salts, precipitation of, by barium chloride in presence of sulphates (Smith), A., ii, 371.
    - ammines (Ephraim and Millmann), A., ii, 320.
    - orthoarsenate, crystalline (Ježek and Simek), A., ii, 491.
    - azide (Wöhler and Martin), A., i, 384.
    - chloride, dialysis of, and preparation of the hydrated oxide (Neidle and Barab), A., ii, 262.
      - compounds of ethyl ether and benzyl sulphide with (Forster, Cooper, and Yarrow), T., 809; A., i, 646.
    - hydroxide, colloidal, physico-chemical analysis of (Pauli and Matula), A., ii, 563.
      - adsorption of sulphuric acid by (Dittler), A., ii, 443.
    - oxide, colloidal hydrated, preparation of (Neidle and Crombie), A., ii, 93.
      - mixtures of alumina and (Scheetz), A., ii, 574.
      - and hydroxide, adsorption of albumin by (Rakuzin), A., ii, 72.
  - **Ferrous** salts, detection of, in body fluids (Popesco), A., ii, 44.
    - titration of, with potassium permanganate (Neidle and Crombie), A., ii, 93.
    - sulphate, conductivity measurements of the action of potassium dichromate and (Edgar), A., ii, 288.
- **Iron**:—
  - **Ferrous** sulphide, heat of formation of (Parravano and de Cesaris), A., ii, 292.
- **Iron organic compounds**:—
  - with acetylacetone and pyridine (Weinland and Bässler), A., i, 6.
  - **Ferric** compounds with salicylic acid (Weinland and Zimmermann), A., i, 649.
    - chloride, compounds of, with unsaturated organic compounds (Gangloff and Henderson), A., i, 533.
    - ferricyanides, colloidal (Haller), A., i, 324.
  - **Cast iron**, estimation of phosphorus in (Cavazzi), A., ii, 540.
  - **Steel**, influence of velocity of cooling on the temperature of transformation and structure of (Portevin and Garvin), A., ii, 372.
    - heterogeneity of (Le Chatelier and Dupuy), A., ii, 535; (Charpy and Bonnerot), A., ii, 573.
    - corrosion of (Aston), A., ii, 161.
    - corrosion and electrical properties of (Hadfield and Newbery), A., ii, 210.
    - tempering of (Le Chatelier), A., ii, 477.
    - transformations of (Dejean), A., ii, 477, 535.
    - magnetic transformation of cementite in (Chevenard), A., ii, 372, 412.
    - estimation of chromium in (Koch), A., ii, 221; (Kelley, Adams, and Wiley), A., ii, 512.
    - estimation of manganese in (Cashmore), A., ii, 43; (Nesbitt), A., ii, 180; (Kinder), A, ii, 389.
    - estimation of molybdenum and vanadium in (Travers), A., ii, 545.
    - estimation of phosphorus in (Friedrich), A., ii, 536.
    - estimation of sulphur in (Pulsifer), A., ii, 100.
    - estimation of tantalum in (Kelley, Myers, and Illingworth), A., ii, 546.
    - See also Magnet steel, Manganese steel, and Tungsten steel.
- **Iron detection, estimation, and separation**:—
  - reduced by hydrogen, analysis of (Winkler), A., ii, 511.
  - detection of, microchemically, in plants (Wiener), A., ii, 44.
  - estimation of (Berg), A., ii, 220.

Iron detection, estimation, and separation:—
  estimation of, volumetrically (Kinder), A., ii, 391.
  estimation of, in glass sand (Ferguson), A., ii, 581.
  estimation of manganese in (Kinder), A., ii, 389.
  estimation of phosphorus in (Friedrich), A., ii, 536.
  estimation of sulphur in (Pulsifer), A., ii, 100.
  separation of aluminium and (Palkin), A., ii, 581.
  separation of lead and (Sacher), A., ii, 272.
Iron ore, estimation of nickel in (Covitz), A., ii, 153.
Iron-rhodonite, artificial, in slags (Tacconi), A., ii, 497.
Isaac of Holland. See Hollandus.
Isatide, constitution of (Kohn), A., i, 175.
Isatin, constitution of the salts of (Heller), A., i, 219, 708; (Claasz), A., i, 413.
Isatol (Heller), A., i, 220.
Isethionic acid, condensation of anaesthesine and (Salkowski), A., i, 305.
Isethionyl-*p*-aminobenzoic acid, physiological behaviour of (Salkowski), A., i, 305.
Isomerisation (Bougault), A., i, 335.
Isomerism (Heller), A., i, 219.
  dynamic, and rotatory dispersion (Patterson), A., ii, 5.
  and polymorphism (Pfeiffer, Klinkert, and v. Pollitzer), A., i, 140.
Isoprene, polymerisation of (Ostromisslenski), A., i, 399.
Isotopes, separation of (Soddy), A., ii, 437.
Ittnerite, composition of (Thugutt), A., ii, 493.

J.

Jadeite, micro-detection of (Cathrein), A., ii, 336.
Jambul tree, constituents of (Hart and Heyl), A., i, 191.
Jellies, formation of (Clowes), A., ii, 245.
  structure of (Moeller), A., ii, 132.
  rhythmic diffusion in (Moeller), A., ii, 410.
  action of aqueous solutions on (Moeller), A., ii, 454.
Ježekite (Slavík and Skarnitzl), A., ii, 145.
Jute. See *Corchorus capsularis.*

K.

Kafir, new protein from (Johns and Brewster), A., i, 108.
Kafirin (Johns and Brewster), A., i, 108.
Kaolinite, decomposition of, by heat (Sokolov), A., ii, 492.
Kelp. See *Nereocystis luetkeana.*
Kephir cells, formation of enzyme in (v. Euler and Griese), A., i, 679.
Keracyanin, and its chloride (Willstätter and Zollinger), A., i, 45.
Kerasin, and its derivatives (Levene and West), A., i, 657.
Ketens (Staudinger and Becker), A., i, 629; (Staudinger and Hirzel), A., i, 630; (Staudinger), A., i, 650; (Staudinger and Endle), A., i, 666.
  polymeric, relationship of, to *cyclo*butane-1:3-diones (Schroeter, Kesseler, Liesche, and Müller), A., i, 145.
Ketendicarboxylic acid, ethyl ester (Staudinger and Hirzel), A., i, 178, 630.
α-Keto-Δ^{β}-butene-αβ-dicarboxylic acid, γ-amino-, ethyl ester (Benary, Reiter, and Soenderop), A., i, 253.
2-Ketodihydronaphthasultam-3:4-phenazine (Zincke and Schürmann), A., i, 40.
3-Keto-1:2-diphenyl-4-ethyltrimethyleneimine-4 carboxylic acid, ethyl ester (Staudinger and Modrzejewski), A., i, 650.
ζ-Keto-βδ-diphenyl-Δ^{α}-octenoic acid, and its semicarbazone (Scholtz), A., i, 463.
ζ-Keto-βζ-diphenyl-δ-styrylheptoic acid, β-hydroxy- (Scholtz), A., i, 463.
Ketohexoses, detection of, with thiobarbituric acid (Plaisance), A., ii, 276.
4-Keto-5-ψ-indoxylidenethiazolidine, 2-imino- (Andreasch), A., i, 664.
β-Keto-α-methylvaleric acid, methyl ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 147.
3-Keto-1:8-naphthasultam-4-quinone, 2:2-*di*chloro- (Zincke and Schürmann), A., i, 40.
Ketones, preparation of (Schicht and Grün), A., i, 443; (Dumesnil), A., i, 653.
  optically active (Rupe and Wild), A., i, 538.
  condensation of aldehydes with (H. and P. Ryan), A., i, 348.
  condensation of pyrrole-2-aldehyde with (Lubrzynska), A., i, 52.

Ketones, action of alcoholic potassium hydroxide on (Montagne), A., i, 35, 143.
aromatic, synthesis of (Hoesch and v. Zarzecki), A., i, 342.
hydrogenation of (Mailhe and de Godon), A., i, 315.
cyclic, preparation of (Schaarschmidt), A., i, 285, 703; (Ullmann), A., i, 342.
unsaturated, action of γ-diketones with (Scholtz), A., i, 462.
α-Ketonic acids, oxidation of the oximes of (Bougault), A., i, 694.
semicarbazones of, and their reactions (Bougault), A., i, 26, 688.
β-Ketonic bases, synthesis of (Mannich), A., i, 634.
4-Keto-3-phenyl-5-benzylidenethiazolidine, 2-imino- (Andreasch), A., i, 663.
α-Keto-β-phenylbutyrolactone, and its derivatives (Hemmerlé), A., i, 394.
4-Keto-1-phenyl-3:6-dimethyl-1:4-dihydropyridazine-5-carboxylic acid (Hale), A., i, 56.
ξ-Keto-β-phenyl-δ-styryloctoic acid, β-hydroxy-, and its derivatives (Scholtz), A., i, 462.
ζ-Keto-ζ-phenyl-β-p-tolyl-δ-styrylheptoic acid, β-hydroxy- (Scholtz), A., i, 463.
ζ-Keto-β-p-tolyl-δ-styryloctoic acid, β-hydroxy- (Scholtz), A., i, 463.
ζ-Keto-βδζ-triphenyl-Δα-heptenoic acid (Scholtz), A., i, 463.
Kidneys, excretion of urea by (Addis and Watanabe), A., i, 103.
Kinetics of chemical reactions (Gerasimov), A., ii, 133.
Kipp's apparatus, modified (Angeli), A., ii, 173.
Kynurenamide. See Quinoline-3-carboxylamide, 4-hydroxy-.

L.

Lacroixite (Slavík and Jílek), A., ii, 145.
Lactacidogen, chemistry of (Embden and Laquer), A., i, 674.
Lacthydroxamic acid, and its potassium salt and benzoyl derivative (Jones and Neuffer), A., i, 326.
Lactic acid, formation of, in blood (Macleod and Hoover), A., i, 426.
formation of, in the liver in diabetes (Embden and Isaac), A., i, 496.
biochemical oxidation of (Mazé and Ruot), A., i, 310.
mercuric salt, preparation of, and stability of its solutions (François), A., i, 114.
Lactic acid, azides and hydrazides of, and their derivatives (Curtius and Aufhäuser), A., i, 636.
detection and estimation of, in biological products (Phelps and Palmer), A., ii, 278.
estimation of, in urine (Mayer), A., ii, 583.
estimation of, in wines (Roettgen), A., ii, 583.
Lactones, catalytic action of acids in formation of (Taylor and Close), A., ii, 253.
Lactose, action of formaldehyde on (Heiduschka and Zirkel), A., i, 446.
Lævulic acid, phenylcarbaminohydrazone of (Borsche), A., i, 118.
p-nitrobenzyl ester (Lyons and Reid), A., i, 559.
Lævulose (d-*fructose; fruit-sugar*), new form of (Irvine and Robertson), A., i, 79.
estimation of, in presence of dextrose (Loewe), A., ii, 49.
estimation of, in mixtures of sugars (Atkins), A., ii, 157.
Laminaria agardhii, influence of metallic salt solutions on the electrical resistance of (Osterhout), A., i, 434.
Lampblack, freezing of water absorbed in (Foote and Saxton), A., ii, 241.
Landolt reaction (Eggert), A., ii, 197.
Lanthanum ferricyanide (Grant and James), A., ii, 316.
Lariscinic acid. See Maltol.
Laterite, formation of, in soils (Stremme), A., i, 512.
Lead, atomic weight of (Œchsner de Coninck), A., ii, 33.
radioactive, atomic weight of (Richards and Wadsworth), A., ii, 91.
atomic weights of isotopes of (Fajans and Lembert), A., ii, 472.
separation of isotopic forms of (Richards and Hall), A., ii, 230.
Röntgen ray spectra of radium-G and (Siegbahn and Stenström), A., ii, 524.
electrode potential of (Günther), A., ii, 439.
electrode potentials of tin and (Noyes and Toabe), A., ii, 438.
solubility of salts of isotopes of (Fajans and Fischler), A., ii, 472.
Lead alloys with sodium in liquid ammonia (Smyth), A., ii, 473.
Lead arsenate, estimation of arsenic in (Gray and Christie), A., ii, 102.
arsenates (McDonnell and Smith), A., ii, 33, 314.

Lead hydrogen arsenate, decomposition of, by water (McDonnell and Graham), A., ii, 534.
chloride, reduction of (Gawalowski), A., ii, 88.
*tetra*chloride, electrolytic preparation of (Kremann and Breymesser), A., ii, 573.
*tetra*fluoride, preparation of (Ruff and Winterfeld), A., ii, 202.
haloids, compounds of, with haloids of substituted ammonium bases (Datta and Sen), A., i, 323.
iodide, thermodynamic properties of silver iodide and (Taylor), A., ii, 14.
solubility of (Denham), T., 29.
*sub*iodide (Denham), T., 29; A., ii, 141.
molybdate, precipitation of (Weiser), A., ii, 105.
nitrate, electrical conductivity of, in pyridine (Mathews and Johnson), A., ii, 289.
*sub*oxide, preparation of (Denham), T., 29; A., ii, 141.
sulphate, solubility of, in sulphuric acid (Ditz and Kanhäuser), A., ii, 208.
reduction of (Perley and Davis), A., ii, 141.
Polyplumbates and polysilicates (Kassner), A., ii, 314.
Lead organic compounds (Möller and Pfeiffer; Pfeiffer, Truskier, and Disselkamp; Grüttner and Krause), A., i, 122.
alkyls, and their derivatives (Grüttner and Krause), A., i, 256, 257, 384.
diethyl dibromide and diphenyldiethyl (Möller and Pfeiffer), A., i, 122.
diethyl-ε-bromoamyl bromide, ethyl-ε-chloroamyl dichloride, triethyl-*n*-amyl, and triethyl-ε-bromoamyl (Grüttner and Krause), A., i, 123.
diphenyl, tri-*n*-butyl and tri-*n*-propyl haloids (Pfeiffer, Truskier, and Disselkamp), A., i, 122.
Lead estimation and separation:—
estimation of (Weiser), A., ii, 105.
estimation of, volumetrically, with ammonium molybdate (Sacher), A., ii, 180.
estimation of, in alloys (Hagmaier), A., ii, 181.
estimation of antimony, copper and (Howden), A., ii, 580.
estimation of, and its separation from antimony (McCabe), A., ii, 333.
separation of iron and (Sacher), A., ii, 272.
Lead electrode. See Electrode.
Leaves, green, carbohydrate metabolism in (Gast), A., i, 433.
variegated, presence of proteins in (Lakon), A., i, 504.
Le Chatelier-Braun principle (Rayleigh), T., 250; A., ii, 236.
Lecithin, supposed existence of, in egg-yolk (Barbieri), A., i, 238.
from ox-heart, hydrolysis of (MacArthur, Norbury and Karr), A., i, 315.
action of cobra poison on (Kudicke and Sachs), A., i, 70.
Lectures, delivered before the Chemical Society (Chapman), T., 203; A., ii, 266; (Pyman), T., 1103.
Lecture experiments, to show the enrichment of illuminating gas (Baker), A., ii, 255.
on the theory of explosives (Eggert and Schimank), A., ii, 462.
to show the preparation of sodium (Wiechowski), A., ii, 568.
Legumin (Rakuzin and Pekarskaja), A., i, 232.
Leifite (Bøggild and Christensen), A., ii, 147.
Leucine anhydride (Graves, Marshall, and Eckweiler), A., i, 358.
Leverrierite from Colorado (Larsen and Wherry), A., ii, 324.
Lichens, constituents of (Hesse), A., i, 457.
used for dyeing (Ryan and O'Riordan), A., i, 342.
carbohydrates of (Tollens), A., i, 618.
See also *Chrysothrix nolitangere.*
d- and *l*-**Lichenidin** (Hesse), A., i, 458.
Lichenoin (Hesse), A., i, 459.
Life, temperature-coefficients of processes of (Osterhout), A., i, 715.
Light, catalytic production of, at low temperatures (Goss; Harvey), A., ii, 436.
emission of, by animals (Trojan), A., i, 427.
absorption of, by inorganic compounds (Brannigan and Macbeth), A., ii, 2.
Light-filter for ultra-violet spectra (Peskov), A., ii, 349.
Lignoceric acid from rotten oak bark (Sullivan), A., i, 8.
Limestone, carbon dioxide from (Lidov), A., ii, 87.
analysis of (Moir), A., ii, 386.
apparatus for estimation of carbonates in (Barker), A., ii, 506.
Lime-sulphur liquids, estimation of sulphur compounds in (Wöber), A., ii, 503.

Linaria, crystalline organic substances in (Molisch), A., i, 506.

Linolenoanilide (de' Conno), A., i, 387.

Linoleno-*p*-toluidide (de' Conno), A., i, 387.

Linoleno-*m*-xylidide (de' Conno), A., i, 387.

Linseed oil, effect of heat and oxidation on (Friend), T., 162 ; A., i, 249.

Lipase, action of (Falk), A., i, 598.
activation of, by cholates (de Jonge), A., i, 362.
hydrolysis of fats by (Tancov), A., i, 182.

Lipoids in blood in anæmia (Bloor and MacPherson), A., i, 609.
adsorption of odour by (Kremer), A., i, 607.

Liquids, constitution and properties of (Langmuir), A., ii, 525.
electric double-layer at the contact of solids and (Frenkel), A., ii, 191.
vapour pressure and density of (Schmidt), A., ii, 406.
surface tension of (Jaeger and Kahn), A., ii, 69, 70, 71 ; (Harkins, Brown, and Davies), A., ii, 238 ; (Harkins, Davies, and Clark), A., ii, 239.
viscosity of (Kendall and Monroe), A., ii, 524, 525.
fluidity and viscosity of (Drucker), A., ii, 409.
diffusion in (Clack), A., ii, 75.
measurement of the dilatation of (Escard), A., ii, 524.
phenomena of suspended transformation in (Kornfeld), A., ii, 129.
anisotropic, chemical reactions in (Svedberg), A., ii, 249, 439.
orientation of, on crystals (Grandjean), A., ii, 451.
mixed, surface tension of (Morgan and Evans), A., ii, 561.
mutual solubility of (Wroth and Reid), A., ii, 17.
organic, molecular diameters of, and their solubility in water (Herz), A., ii, 195.
mixed, analysis of (Atkins), A., ii, 47.
pure, molecular state of (Pavlov), A., ii, 125, 293, 358.

Liquorice, estimation of glycyrrhizin in (Linz), A., ii, 430.

Lithium alloys with mercury, electrical conductivity of (Hine), A., ii, 287.

Lithium carbonate (Seyler and Lloyd), T., 994 ; A., ii, 571.
chloride, melting point of, and freezing points of its mixtures with alkali chlorides (Richards and Meldrum), A., ii, 531.
solubility of, in mixed non-aqueous solvents (Marden and Dover), A., ii, 243.
nitrate, electro-reduction of (Kliatchko and Binggely), A., ii, 355.

Lithium organic compounds :—
ethyl, methyl, and phenyl (Schlenk and Holtz), A., i, 256.

Lithium estimation and separation :—
estimation of, in water (Averitt), A., ii, 423.
separation of, from potassium and sodium (Palkin), A., ii, 43.

Lithium atom, structure and internal electric field of (Hartmann), A., ii, 206.

Lithofellic acid, constitution of (Fischer), A., i, 4.

Liver, effect of reaction of the medium on autolysis of (Morse), A., i, 526.
oxidation of alcohol by (Hirsch), A., i, 67.
glycogen content of (McDanell and Underhill), A., i, 364.
formation of lactic acid and acetoacetic acid in, in diabetes (Embden and Isaac), A., i, 496.
polysaccharide in the blood from (Macleod), A., i, 524.
formation of sugar in (Baldes and Silberstein), A., i, 673.
formation of urea in (Clementi), A., i, 674.

Lorettoite (Wells and Larsen), A., ii, 96.

Lucerne (*alfalfa*), effect of phosphorus compounds on the growth of, and its bacteria (Truesdell), A., i, 242.

Lucerne hay, stachydrin from (Steenbock), A., i, 439.

Luciferin in luminous bacteria (Harvey), A., i, 365.

Lutidinium palladi- and pallado-chlorides (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.

Lutidone, *di*iodo-, and its hydrochloride (Datta and Prosad), A., i, 332.

Lysine, reaction of nitrous acid with (Sure and Hart), A., ii, 551.

Lyxose, preparation of (Clark), A., i, 632.

M.

Maclurin, preparation of (Hoesch and v. Zarzecki), A., i, 342.

Magnesium, arc spectrum of (Catalán Sañudo), A., ii, 161.
  action of, on water and on solutions of potassium chloride (Getman), A., ii, 90, 258.
  excretion of, in urine (Nelson and Burns), A., i, 104.
Magnesium carbonate (Seyler and Lloyd), T., 994; A., ii, 571.
  oxide (*magnesia*), refractory properties of (Le Chatelier and Bogitch), A., ii, 573.
    action of silica with (Hedvall), A., ii, 205.
    calcined, examination of purity of (Astruc), A., ii, 508.
  pyrophosphate, colour of, after ignition (Balareff), A., ii, 90.
  sulphate, mixed crystals of zinc sulphate and (Viola), A., ii, 79.
  potassium sulphate, solubility of (van Klooster), A., ii, 471.
Magnesium organic compounds, reactions of esters with (Stadnikov), A., i, 136.
Magnesium, estimation of (Busvold), A., ii, 218.
  estimation of, volumetrically, in water (Bruckmiller), A., ii, 271.
Magnet steel, structure of (Honda and Murakami), A., ii, 535.
Maize, effect of, on growth and development (McCollum, Simmonds, and Pitz), A., i, 185.
  dietary deficiencies of (McCollum, Simmonds, and Pitz), A., i, 192; (Hogan), A., i, 363.
  as a diet and its influence on pellagra (Suárez), A., i, 69.
Maize silage, occurrence and significance of mannitol in (Dox and Plaisance), A., i, 683.
Malachite, pseudomorphs of (Liesegang), A., ii, 489.
Malachite-green, 4-*mono*-, and 2:4-*di*-hydroxy- (Ghosh and Watson), T., 826.
Maleic acid, *p*-nitrobenzyl ester (Lyman and Reid), A., i, 334.
Malic acid, fermentation of (Lebedev), A., i, 188.
  metallic salts, injection and elimination of (Wise), A., i, 105.
  azide and hydrazide of, and their derivatives (Curtius and v. Hofe), A., i, 637.
  p-nitrobenzyl esters (Lyman and Reid), A., i, 334.
Malonanilic acid, and bromo-, esters of (Staudinger and Becker), A., i, 630.
  m- and *p*-amino-, and *m*- and *p*-nitro-, derivatives of (Jacobs and Heidelberger), A., i, 583.
Malonic acid, salts of, electrolysis of (Schall), A., ii, 118.
  reactions between bisulphite compounds of unsaturated aldehydes and (Nottbohm), A., i, 27.
  p-nitrobenzyl ester (Reid), A., i, 334.
Malon-*p*-toluidic acid, ethyl ester (Staudinger and Becker), A., i, 630.
Malonylguanidine, barbituric acid and thiobarbituric acid, use of, in estimation of furfuraldehyde (Dox and Plaisance), A., ii, 53.
Malt, influence of hydrion concentration on activity of diastase of (Adler), A., i, 61.
  amylase of, effect of bromides on action of (Thomas), A., i, 598.
    hydrolysis of starch by (Sherman and Walker), A., i, 597.
Maltol, crystallography of (Steinmetz), A., i, 580.
Maltose, turbidity of solutions of, and of their mixtures with dextrose (Homberger and Marvel), A., i, 370.
  action of formaldehyde on (Heiduschka and Zirkel), A., i, 446.
Mandelamideglucosides (Fischer and Bergmann), A., i, 658.
Mandelhydroxamic acid, and its benzoyl derivative (Jones and Neuffer), A., i, 326.
d-**Mandelonitrile-glucoside** (*sambunigrin*), synthesis of (Fischer and Bergmann), A., i, 658.
Manganese in flowers and stems (McDonnell and Roark), A., i, 720.
Manganese alloys with gold (Hahn and Kyropoulos), A., ii, 476.
Manganese compounds, estimation of the available oxygen in (Barnebey and Hawes), A., ii, 274.
Manganese salts, content of, in plants (Ehrenberg and Nolte), A., i, 504.
Manganese *di*oxide, colloidal, physical properties of (Witzemann), A., ii, 262.
  Manganic compounds, constitution of (Sem), A., ii, 319.
  Manganous azide (Wöhler and Martin), A., i, 384.
Manganese organic compounds (Verkade), A., i, 377.
Manganese detection and estimation:—
  detection of (Macri), A., ii, 511.
  estimation of (Travers), A., ii, 511.
Manganese, estimation of, electrolytically (Gooch and Kobayashi), A., ii, 425.
  estimation of, in presence of iron (Barnebey and Bishop), A., ii, 390.

Manganese, estimation of, in iron and steel (Kinder), A., ii, 389.
  estimation of, in steel (Cashmore), A., ii, 43; (Nesbitt), A., ii, 180.
Manganese steel (Portevin), A., ii, 415; (Dejean), A., ii, 477.
Mannitol, occurrence and significance of, in maize silage (Dox and Plaisance), A., i, 683.
Manno-aldo- and -keto-heptose, properties of (Wright), A., i, 119.
d-**Mannoketoheptose**, and its derivatives (La Forge), A., i, 118.
Mannonic acid, hydrazides of (Weerman), A., i, 548.
Mannose, preparation and mutarotation of (Hudson and Sawyer), A., i, 321.
d-**Mannose-*p*-tolylhydrazone** (van der Haar), A., i, 380.
Manures, use of superphosphates as (Barbieri), A., i, 312.
  artificial, application of, to carnations (Beal and Muncie), A., i, 190.
    nitrogenous, relative value of (Lipman and Burgess), A., i, 243.
  estimation of nitrogen in (Lagers), A., ii, 329.
Manurial experiments in soils (de Wilkoszewski), A., i, 723.
Maplewood, constituents of creosote from (Pieper, Acree, and Humphrey), A., i, 452.
Margarine, nutritive value of (Halliburton and Drummond), A., i, 673.
Marsh mallow (*Radix althaeae*), colloidal solutions from the roots of (Gutbier and Weise), A., ii, 21, 131.
Martensite, formation of (Dejean), A., ii, 477, 535.
Matter, energy theory of (Redgrove), A., ii, 411.
Meat extracts, detection and estimation of formic acid in (Waser), A., ii, 343.
  estimation of sugar in (Smith), A., ii, 49.
Meconic acid, constitution of (Borsche), A., i, 117.
Mecocyanin, and its salts (Willstätter and Weil), A., i, 49.
Melilite, constitution of (Clarke), A., ii, 417.
Mellitic acid, occurrence of (v. Lippmann), A., i, 272.
  p-nitrobenzyl ester (Lyons and Reid), A., i, 559.
Melting points of homologous organic compounds (Tammann), A., ii, 441.
  of hydrocarbons (Enklaar), A., i, 113.
Melting-point curves of mixtures (Parravano and Mazzetti), A., ii, 292.
Melting-point determinations, at low temperatures (Stock), A., ii, 192.
Membranes for dialysis, preparation of (Brown), A., ii, 362.
  animal. See Animal membranes.
  copper ferrocyanide, properties of (Tinker), A., ii, 363.
  semi-permeable, and osmosis (Bancroft), A., ii, 444.
Menhaden oil, analysis of the fatty acids of (Twitchell), A., ii, 428.
Menthanecarboxylic acids (Kursanov), A., i, 137.
Menthol, crystallisation of (Wright), A., i, 576.
l-**Menthone**, inversion of, by lithium, potassium and sodium ethoxides (Gruse and Acree), A., ii, 251.
Menthyl chloride, crude, composition of (Kursanov), A., i, 151.
d-**Menthyl** iodide (Kursanov), A., i, 396.
α- and β-**Menthylglucosides**, and their derivatives (Fischer and Bergmann), A., i, 468.
Menthylphenols (Kursanov), A., i, 396.
Menthylphenyl phenyl ether (Kursanov), A., i, 397.
Mercaptans, esterification of acetic and propionic acids by (Faber and Reid), A., i, 626.
Mercury, spectrum of (Richardson and Bazzoni), A., ii, 521.
  colloidal (Gutbier and Wagner), A., ii, 169.
    rhythmic precipitation of (Davis), A., ii, 452.
  apparatus for distillation of (Duschak and Spencer), A., ii, 316.
  apparatus for purification of (Patten and Mains), A., ii, 413; (Dunnicliffe), A., ii, 414.
Mercury alloys (*amalgams*), liquid, interaction of salt solutions with (Smith and Ball), A., ii, 247.
  with lithium, potassium and sodium, electrical conductivity of (Hine), A., ii, 287.
Mercury salts, luminescence of (Weiser), A., ii, 174.
Mercury:—
  Mercuric salts, velocity of reduction of (Linhart and Adams), A., ii, 301.
    chloride, solubility of, in mixed non-aqueous solvents (Marden and Dover), A., ii, 243.
      action of, on colloidal gold solutions (Herstad), A., ii, 168.
    iodide, allotropy of (Smits), A., ii, 174; (Tammann), A., ii, 474.

- **Mercury**:—
  - **Mercuric** iodide, solubility of, in pyridine (Mathews and Ritter), A., ii, 300.
    - reactions brought about by (Hartley), A., i, 82.
  - oxide, yellow, as a standard in alkalimetry (Incze), A., ii, 327.
  - sulphide, action of ammonium monosulphide with (Christensen), A., ii, 33.
  - **Dimercuric** *di*iododisulphide (Rây), T., 109; A., i, 194.
  - **Mercurous** chloride (*calomel*) electrode. See Electrode.
- **Mercury organic compounds** (Rupp and Herrmann), A., i, 516.
  - complexity of (Biilmann and Hoff), A., i, 123.
  - use of, as disinfectants (Schrauth and Schoeller), A., i, 241.
  - with unsaturated acids (Biilmann and Hoff), A., i, 123.
  - with thiophen (Steinkopf), A., i, 302.
  - estimation of nitrogen in (Justin-Mueller), A., ii, 39.
  - 5:5′-dibromo-2:2′-dithienyl (Steinkopf), A., i, 303.
  - 5:5′-dichloro-2:2′-dithienyl (Steinkopf), A., i, 303.
  - 5:5′-di-iodo-2:2′-dithienyl (Steinkopf), A., i, 302.
  - mercaptide nitrites, and their reaction with alkyl iodides (Rây), T., 101; A., i, 194.
  - tetramethyldithienyls (Steinkopf), A., i, 303.
  - **Mercuric** nitrite, compounds of alkaloids with (Rây), T., 507; A., i, 470.
    - compounds of thiocarbamides and (Rây), T., 106; A., i, 194.
  - oxycyanide, estimation of, volumetrically (Tagliavini), A., ii, 510.
  - **Mercurous** haloids, compounds of, with haloids of substituted ammonium bases (Datta and Sen), A., i, 323.
  - **Mercuriallylmaleic acid**, hydroxy-, anhydride (Biilmann and Hoff), A., i, 124.
  - **Mercuric 2:4:6-*tri*bromophenoxide** (Rupp and Herrmann), A., i, 517.
  - **Mercuriphenol-*p*-sulphonic acid**, 2:6-*di*chloro-, and 2:6-*di*hydroxy-, and their salts (Rupp and Herrmann), A., i, 488.
  - **Mercurithymol**, 2:6-*di*-chloro-, -hydroxy-, and -iodo- (Rupp), A., i, 670.
- **Mercury detection and estimation**:—
  - detection of (Bräuer), A., ii, 509.
  - detection of, for forensic purposes (Spica), A., ii, 543.
  - detection of traces of, in toxicology (Browning), T., 236; A., ii, 272.
  - estimation of, in galenical preparations (Wastenson), A., ii, 509.
  - estimation of, in organic compounds (Marsh and Lye), A., ii, 219; (Lomholt and Christiansen), A., ii, 424.
  - estimation of, in pharmaceutical preparations (Herrmann), A., ii, 399.
  - estimation of, in basic mercury salicylate (Lajoux), A., ii, 273.
- **Mercury electrode.** See Electrode.
- **Mesoxalic acid**, basic bismuth salt, and comparison of the phenylhydrazone with phenylhydrazine oxalate (Evans, Mong, and Sinks), A., i, 595.
- **Mesoxamide semialdehyde**, derivatives of (Dakin), A., i, 543.
- **Metabolism** and bioluminescence (Heller), A., i, 427.
  - of aromatic acids (Sherwin), A., i, 603.
  - calcium (Paul and Sharpe), A., i, 66; (Givens and Mendel; Givens), A., i, 603.
  - carbohydrate (McDanell and Underhill), A., i, 359, 364, 368.
    - in green leaves (Gast), A., i, 433.
  - of dextrose in surviving organs (Lombroso), A., i, 102; (Artom), A., i, 186.
  - of fats (Lyman), A., i, 714.
  - gaseous, effect of ethyl alcohol on, in man (Higgins), A., i, 489.
  - of guinea-pigs (Smith and Lewis), A., i, 714.
  - magnesium (Givens and Mendel; Givens), A., i, 603.
  - nitrogen, influence of cystine on (Lewis), A., i, 603.
    - in plants (Prianichnikov), A., i, 616.
  - phosphorus, influence of extract of genital glands on (Jean), A., i, 304.
  - in phosphorus poisoning (Isaac; Isaac and Loeb), A., i, 678.
  - purine, biochemistry of (Hunter), A., i, 184.
    - after administration of poisons (Pohl), A., i, 498.
  - sulphur, influence of, on the nitrogen balance (Lewis), A., i, 603.
- **Metallic** chlorides, crystallisation in ternary systems of (Liebisch), A., ii, 248.
  - cyanides, reaction of methyl iodide with (Hartley), A., i, 83.

Metallic films, obtained by evaporation in vacua (Reinders and Hamburger), A., ii, 405.
prepared by the spraying method (Arnold), A., ii, 260.
haloids, compounds of arsenious oxide and (Schreinemakers and de Baat), A., ii, 173.
compounds of ethers with, and their decomposition products (Conev), A., i, 135.
oxides, potential measurements with (Baur, Petersen, and Füllemann), A., ii, 116; (Treadwell), A., ii, 117.
influence of the size of particles of, on the velocity of solution in acids (Podszus), A., ii, 300.
action of sulphur dioxide on (Hammick), T., 379; A., ii, 306.
*per*oxides, action of nitric oxide on (Dutt and Sen), A., ii, 85.
salts, electrical conductivity of, in pyridine (Mathews and Johnson), A., ii, 289.
electrolytic dissociation of (Sachanov), A., ii, 115.
heated, positive ionisation of (Waterman), A., ii, 162.
complex, constitution of, from mobility and conductivity (Lorenz and Posen), A., ii, 14, 439.
freezing-point lowerings in solutions of, and their mixtures (Hall and Harkins), A., ii, 65; (Harkins and Roberts), A., ii, 66.
viscosity of solutions of (Herz), A., ii, 361.
purification of, by clarification or by fractional crystallisation (Rengade), A., ii, 451.
solubilities of, in *iso*amyl alcohol solution (Curtis and Burns), A., ii, 260.
interaction of solutions of, and liquid amalgams (Smith and Ball), A., ii, 247.
reduction of, by organic acids, in presence of oxidising agents (Dhar), T., 690; A., ii, 458.
effect of hydrochloric acid on the excretion of, in dogs (Stehle), A., i, 609.
sulphates, decomposition of, by heat (Hofman and Wanjukow), A., ii, 465.
estimation of, electro-volumetrically (Harned), A., ii, 272.
sulphides, influence of hydrogen sulphide on the stability of colloidal solutions of (Young and Goddard; Young and Neal), A., ii, 167.
Metals, preparation of, in a metalloid condition (v. Weimarn), A., ii, 315.
arc and spark spectra of (Takamine and Nitta), A., ii, 402.
galvanic ennobling of (van Deventer), A., ii, 11.
overvoltage of (Newbery), T., 470; A., ii, 355.
polymorphous, thermo-electric properties of (Laschtschenko, Bykov, and Efremov), A., ii, 114.
passivity of (Bennett and Burnham), A., ii, 209; (Stapenhorst), A., ii, 290.
properties of solid solutions of, and their alloys (Thompson), A., ii, 481.
cooling of, by immersion in water (Garvin and Portevin), A., ii, 291.
and their alloys, surface tension of (Smith), A., ii, 408.
velocity of crystallisation of (Czochralski), A., ii, 302.
velocity of solution of (Centnerszwer), A., ii, 135.
colloidal, preparation of, by means of citarine (Vanino), A., ii, 299.
preparation of solutions of (Zsigmondy, Hiege, and Reitstötter), A., ii, 364.
and their alloys, chemistry of (Gillett), A., ii, 80.
action of potassium permanganate on (Foster), A., ii, 175.
action of sulphur chloride on (Domanicki), A., ii, 369.
Metasaccharinic hydrazide (Weerman), A., i, 548.
Meteoric iron (Merrill and Whitfield), A., ii, 150.
Meteorite, from Brahin (Ivanov; Timoféev), A., ii, 498.
Meteorites, radioactivity of (Quirke and Finkelstein), A., ii, 576.
Methane, electrical ignition of mixtures of air and (Wheeler), T., 411; A., ii, 300.
Methane, chloro-derivatives, preparation of, from natural gas (Bedford), A., i, 77.
iodo-derivatives, ultra-violet absorption spectra of (Massol and Faucon), A., ii, 283.
nitro-, preparation of, and its homologues (Krause), A., i, 377.
Methoxide, sodium, action of halogen-substituted acids with (Madsen), A., ii, 250.
6-Methoxy-5-aldehydo-*p*-xylene, 1-hydroxy- (Sonn), A., i, 143.
1-Methoxy-3-azo-β-naphthol, 4:5-*di*-nitro-2-hydroxy- (Gibson, Simonsen, and Rau), T., 82; A., i, 204.

Methoxybenzoic acids, amino-, and nitro-, and their derivatives (SIMONSEN and RAU), T., 224; A., i, 336.

p-**Methoxybenzophenone**, additive compound of perchloric acid and (PFEIFFER, JOWLEFF, FISCHER, MONTI, and MULLY), A., i, 209.

3'-Methoxybenzophenone, 2:4:4'-*tri*- and 2:4:6:4'-*tetra*-hydroxy- (HOESCH and V. ZARZECKI), A., i, 343.

4-Methoxybenzophenone, 3-bromo- (KOHLER and CONANT), A., i, 570.

o-**Methoxybenzoylphenylethylene** oxide (JÖRLANDER), A., i, 345.

p-**Methoxybenzylideneazobenzene-*p*-hydrazone** hydrochloride (TRÖGER and PIOTROWSKI), A., i, 669.

Methoxybenzylidenemalonylthiocarbamide, and 4-hydroxy- (DOX and PLAISANCE), A., i, 53.

7-Methoxychromanone. See 7-Methoxy-2:3-dihydro-γ-benzopyrone.

7-Methoxychromone, preparation of, and its semicarbazone (PFEIFFER and GRIMMER), A., i, 662.

p-**Methoxycinnamylidenemethyl methyl ketone** (PFEIFFER, JOWLEFF, FISCHER, MONTI, and MULLY), A., i, 209.

4'-Methoxydeoxybenzoin, 2:4-*di*nitro-, and its derivatives (PFEIFFER, JOWLEFF, FISCHER, MONTI, and MULLY), A., i, 207.

7-Methoxy-2:3-dihydro-γ-benzopyrone, and its derivatives, and 3-oximino- (PFEIFFER and GRIMMER), A., i, 662.

Methoxydihydroberberine (G. M. and R. ROBINSON), T., 967.

5-Methoxy-4:5-dihydrouric acid, 4-hydroxy- (BILTZ and HEYN), A., i, 286.

6-Methoxy-α- and -β:3-dimethylcinnamic acids, and their methyl esters (V. AUWERS), A., i, 267.

5-Methoxy-1:3-dimethyl-4:5-dihydrouric acid, 4-hydroxy- (BILTZ and STRUFE), A., i, 297.

5-Methoxy-1:3-dimethyl-ψ-uric acid (BILTZ and STRUFE), A., i, 297.

5-Methoxy-1:7-dimethyl-ψ-uric acid (BILTZ and DAMM), A., i, 295.

5-Methoxy-1:3-dimethyl-$\Delta^{4(9)}$-*iso*uric acid (BILTZ and STRUFE), A., i, 296.

2-Methoxydiphenyl, 5-nitro- (BORSCHE and SCHOLTEN), A., i, 390.

8-Methoxy-1-ethyltheobromine (BILTZ and MAX), A., i, 590.

3'-Methoxyflavone, 5:7:4'-*tri*hydroxy-, and its triacetyl derivative (OESTERLE and KUENY), A., i, 703.

5-Methoxyhydantoin-5-carboxylic acid, methyl ester (BILTZ and HEYN), A., i, 286.

4-Methoxy-2-methylbenzophenonesulphone, 1-chloro- (ULLMANN and V. GLENCK), A., i, 162.

o-**Methoxy-β-methylcinnamic acids**, stereoisomeric, and their derivatives (STOERMER, GRIMM, and LAAGE), A., i, 648.

5-Methoxy-3- and -9-methyl-4:5-dihydrouric acids, 4-hydroxy- (BILTZ and HEYN), A., i, 292.

6-Methoxy-1-methyl-1:2:3:4-tetrahydroquinoline, and its derivatives (V. BRAUN and KINDLER), A., i, 164.

4-Methoxy-3-methylthioltoluene, and 5-bromo-, and its dibromide (ZINCKE and ARNOLD), A., i, 264.

4-Methoxy-2-methylthioxanthone, and 1-amino-, and 1-chloro- (ULLMANN and V. GLENCK), A., i, 161.

4-Methoxy-2-methylthioxanthonyl-1-anthranilic acid (ULLMANN and V. GLENCK), A., i, 161.

5-Methoxy-1-methyl-ψ-uric acid (BILTZ and STRUFE), A., i, 294.

5-Methoxy-9-methyl-ψ-uric acid (BILTZ and HEYN), A., i, 291.

4-Methoxymethylveratrole, 6-bromo-5-nitro- (JONES and ROBINSON), T., 923.

2- and 4-Methoxy-1-naphthylacetic acids (MAUTHNER and MIKA), A., i, 337.

β-4-Methoxy-1-naphthylethylcarbamic acid, ethyl ester (WINDAUS and BERNTHSEN-BUCHNER), A., i, 690.

β-4-Methoxy-1-naphthylpropionic acid, and its derivatives (WINDAUS and BERNTHSEN-BUCHNER), A., i, 690.

2-Methoxy-1-naphthylpyruvic acid (MAUTHNER and MIKA), A., i, 337.

6-Methoxyphenoxyacetic acid, 4-amino-, and its derivatives (JACOBS and HEIDELBERGER), A., i, 697.

o-**Methoxyphenylacetaldehyde**, and its derivatives (WEERMAN), A., i, 560.

α-Methoxyphenyl-acetamide and **-acetonitrile** (HESS and DORNER), A., i, 337.

3-Methoxyphenylacetic acid, α-amino-4-hydroxy- (BLOCH), A., i, 675.

α-Methoxyphenylacetyl chloride (HESS and DORNER), A., i, 337.

p-**Methoxyphenylauramine** (STAUDINGER and ENDLE), A., i, 666.

3-*o*-Methoxyphenyl-2-benzylquinoxaline (JÖRLANDER), A., i, 345.

3-Methoxyphenylethyl methyl ketone, 4-hydroxy-. See Zingerone.

2-*p*-Methoxyphenyl-3-α-hydroxy-α-phenylpropyl*cyclo*propane-1:1-dicarboxylic acid, 2-*m*-bromo-, methyl ester (KOHLER and CONANT), A., i, 570.

o-**Methoxyphenyl ω-hydroxystyryl ketone** (JÖRLANDER), A., i, 345.

3-Methoxyphenylpropionic acid, α-amino-β-4-hydroxy- (BLOCH), A., i, 675.

6-Methoxy-1:2-pyrone-3-carboxylic acid, 4-hydroxy-, methyl ester (STAUDINGER and BECKER), A., i, 630.

2-Methoxyquinoline, 6-*mono*- and 6:8-*di*-nitro- (KAUFMANN and DE PETHERD), A., i, 355.

6-Methoxy-4-quinolylacetic acid, and bromo-, ethyl esters, and their hydrobromides (RABE, PASTERNACK, and KINDLER), A., i, 284.

6-Methoxy-4-quinolyl bromomethyl ketone, and its hydrobromide (RABE, PASTERNACK, and KINDLER), A., i, 284.

α-**6-Methoxy-4-quinolyl-β-piperidinoethyl alcohol** (RABE, PASTERNACK, and KINDLER), A., i, 284.

6-Methoxy-4-quinolyl piperidinomethyl ketone, and its hydrobromide (RABE, PASTERNACK, and KINDLER), A., i, 284.

Methoxystilbenes, and their **carboxylic acids**, and nitro- and nitrocyano-derivatives, and their salts (PFEIFFER, KLINKERT, and v. POLLITZER), A., i, 140.

2-*p*-Methoxystyrylbenziminazole, 5-nitro-2-*m*-hydroxy- (KYM and JURKOWSKI), A., i, 176.

Methoxystyrylcarbamic acids, methyl esters (WEERMAN), A., i, 560.

p-**Methoxystyryl** *p*-**methoxycinnamylideneméthyl ketone**, and its derivatives (PFEIFFER, JOWLEFF, FISCHER, MONTI, and MULLY), A., i, 209.

o-**Methoxystyryl methyl ketone** (v. AUWERS), A., i, 267.

4-Methoxytoluene-3-sulphinic acid, methyl ester (ZINCKE and ARNOLD), A., i, 264.

5-Methoxy-3:7:9-trimethyl-4:5-dihydrouric acid, 4-hydroxy- (BILTZ and DAMM), A., i, 299.

5-Methoxy-1:3:7-trimethyl-ψ-uric acid (BILTZ and HEYN), A., i, 298.

p-**Methoxytriphenylcarbinol**, perchlorate of (PFEIFFER, JOWLEFF, FISCHER, MONTI, and MULLY), A., i, 210.

2-Methoxy-2:4:6-triphenylpyran (DILTHEY), A., i, 579.

5-Methoxy-ψ-uric acid (BILTZ and HEYN), A., i, 286.

6-Methoxy-*p*-xylene, 2-nitro- (SONN), A., i, 143.

Methyl alcohol, occurrence and estimation of, in plants (v. FELLENBERG), A., i, 616.
  vapour pressures of mixtures of carbon disulphide and (BÜCHNER and PRINS), A., ii, 441.

Methyl alcohol, action of phosphoryl chloride on (BALAREFF), A., i, 625.
  detection of (MANNICH and GEILMANN), A., ii, 392.
  detection and estimation of (ELVOVE), A., ii, 341.

Methyl bromomalonyl chloride (STAUDINGER and BECKER), A., i, 630.
  iodide, reaction of metallic cyanides with (HARTLEY), A., i, 83.
    velocity of reaction of, with metallic ethoxides (BROWN and ACREE), A., ii, 24.
  malonyl chloride, and its derivatives (STAUDINGER and BECKER), A., i, 630.
  sulphate, action of aniline on (SHEPARD), A., i, 19.
  potassium sulphate, rate of hydrolysis of (ZAWIDZKI and ZAYKOWSKI), A., ii, 84.
  tellurate (PELLINI), A., i, 2.

Methylamine, preparation of (WERNER), T., 844; A., i, 632.
  physical constants of (BERTHOUD), A., ii, 237.

2-Methylaminobenzoic acid, 3:5-*di*nitro- (KAUFMANN and DE PETHERD), A., i, 355.

γ-**Methylaminobutylbenzene**, and γ-cyano-, and their derivatives (v. BRAUN and NEUMANN), A., i, 283.

p-**Methylamino-*p*′-cyanomethylaminodiphenylmethane** (v. BRAUN), A., i, 174.

p-**Methylamino-*p*′-cyanomethylaminodi-*o*-tolylmethane** (v. BRAUN), A., i, 174.

2-Methylaminoethyl-6-methoxy-4:5-methylenedioxybenzyl bromide, 2-β-cyano- (v. BRAUN), A., i, 163.

2-Methylaminoethyl-4:5-methylenedioxybenzyl bromide, 2-β-cyano-, and its derivatives (v. BRAUN), A., i, 163.

α-**Methylamino-β-methylpentan-γ-one**, and its platinichloride (MANNICH), A., i, 635.

2-Methylaminophenyl-4-methylamino-*m*-tolylmethane, 2-cyano-, and its derivatives (v. BRAUN), A., i, 174.

4-Methylamino-6-phenyl-1:2-pyrone, and its 3-acetyl derivative (KNUST and MUMM), A., i, 415.

4-Methylamino-6-phenyl-1:2-pyrone-3-carboxylic acid (KNUST and MUMM), A., i, 415.

5-Methylamino-ψ-uric acid (BILTZ and HEYN), A., i, 287.

Methylaniline, preparation of (MORGAN), A., i, 197.

Methylaniline, *tetra*nitro-. See **Phenylmethylnitroamine**, *tri*nitro-.

Methylanthraquinones, hydroxy-, in plants (Tunmann), A., i, 531.

*tetra*hydroxy-, and its derivatives (Seel, Kelber, and Scharf), A., i, 577.

Methylation by means of formaldehyde (Werner), T., 844; A., i, 632; (Morgan), A., i, 197.

4-Methylbenzophenonesulphone, 1-chloro- (Ullmann and v. Glenck), A., i, 162.

4-Methylbenzosulphone-2:1-acridone (Ullmann and v. Glenck), A., i, 162.

5-Methylbenz*iso*oxadiazole, preparation of (Green and Rowe), T., 619; A., i, 519.

Methylbixin ozonide, products of decomposition of (Rinkes and van Hassett), A., i, 660.

1-Methyl-3-*tert.*-butylbenzene, *di*amino-hydroxy- and 2:4:6-*tri*amino-, and their derivatives (Herzig, Wenzel, and Taigner), A., i, 177.

Methylcarbamide, amino-, hippuryl derivative, derivatives of (Curtius and Petridis), A., i, 201.

Methylcarbamidoacetic acid, amino-, benzoyl derivative. See Hippenylcarbamidoacetic acid.

hippuryl derivative, and its salts and derivatives (Curtius and Petridis), A., i, 201.

Methylcarbimide, amino-, hippuryl derivative (Curtius and Petridis), A., i, 201.

1-Methyl-1-*di*chloromethyl-$\Delta^{2:5}$-*cyclo*hexadien-4-one, oxime of (v. Auwers), A., i, 34.

1-Methyl-1-*di*chloromethyl-4-*n*-propyl-$\Delta^{2:5}$-*cyclo*hexadien-4-ol (v. Auwers), A., i, 34.

1-Methyl-1-*di*chloromethyl-2-*iso*propyl-Δ^{5}-*cyclo*hexen-4-one, and its derivatives (v. Auwers), A., i, 35.

Methylchavicol, polymerisation of (van Romburgh and van der Zanden), A., i, 690.

Methylcinnamic acids, stereoisomeric, and their derivatives (Stoermer, Grimm, and Laage), A., i, 648.

Methylcodeine, derivatives of (Mannich), A., i, 473.

3-Methylcoumarin periodide (Simonis), A., i, 706.

α-Methylcoumarones, preparation of (Farbenfabriken vorm. F. Bayer & Co.), A., i, 50.

θ-Methyldecoic acid (Levene and Allen), A., i, 4.

4′-Methyldeoxybenzoin, 2:4-*di*nitro-, and its derivatives (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 207.

4-Methyldibenzophenonedisulphone (Ullmann and v. Glenck), A., i, 162.

1-Methyl-4:5-dihydrouric acid, 4:5-*di*hydroxy- (Biltz and Strufe), A., i, 294.

Methyldi-γ-ketobutylamine, and its salts (Mannich), A., i, 634.

Methyl-2:3-diketodihydrothionaphthen (Stollé), A., i, 91.

Methyldi-γ-keto-β-methylamylamine, and its salts (Mannich), A., i, 635.

1-Methyl-2:5-dimethylolpyrrole (Tschelincev and Maksorov), A., i, 165.

4-Methyldithioxanthone (Ullmann and v. Glenck), A., i, 161.

Methylemetine, and its salts (Pyman), T., 444; A., i, 410.

Methylemetinemethine, and its salts (Pyman), T., 445.

Methyleneaminoacetic acid, salts of (Franzen and Fellmer), A., i, 687.

Methyleneaminopropionic acids, and their salts (Franzen and Fellmer), A., i, 687.

Methyleneasparagine, salts of (Franzen and Fellmer), A., i, 687.

Methylene-azure, preparation of (Tribondeau and Dubreuil), A., i, 285.

Methylene-blue colouring matters (Kehrmann, Robert, and Sandoz), A., i, 226.

Methylenecamphoracetic acid. See β-Camphorylidenepropionic acid.

3:4-Methylenedioxybenzylidenemalonylthiocarbamide (Dox and Plaisance), A., i, 53.

5-*mp* Methylenedioxybenzylidene*iso*thiohydantoin (Stieger), A., i, 173.

5:6-Methylenedioxy-2-methylbenziminazole, and its salts (Jones and Robinson), T., 916.

1:2-Methylenedioxyphenanthraphenazine (Jones and Robinson), T., 927.

4-chloro- (Orr, Robinson, and Williams), T., 951.

3:4-Methylenedioxystyryl methyl ketone, 6-chloro- (Orr, Robinson, and Williams), T., 948.

Methyleneglycylglycine, and its barium salt (Franzen and Fellmer), A., i, 687.

Methylenephenylalanine, and its salts (Franzen and Fellmer), A., i, 687.

Methylenesaccharic acid, behaviour of, in the organism (Paderi), A., i, 716.

Methylene-violet, preparation of (Tribondeau and Dubreuil), A., i, 285.

5-Methyl-4-α-ethoxyethyl-6-pyrimidone, 2-thio- (Johnson and Hadley), A., i, 667.

5-Methyl-4-α-ethoxyethyl-6-pyrimidone-2-thiolacetic acid (Johnson and Hadley), A., i, 667.

Methylethylacetophenoneoxime (Dumesnil), A., i, 654.

Methylethylalloxan (Biltz and Max), A., i, 591.

Methylethylenediamine, and its salts (Johnson and Bailey), A., i, 9.

1-Methyl-3-ethylhydantoylmethylamide, and 5-hydroxy- (Biltz and Bergius), A., i, 589.

Methyl ethyl ketone, condensation of pyrrole with (Tschelincev and Tronov), A., i, 411.

4-Methyl-3-ethylpiperidine, 4-amino-, and its derivatives (Rabe and Pasternack), A., i, 217.

4-Methyl-α-ethylstyrene, β-chloro- (v. Auwers), A., i, 34.

Methylethylvioluric acid, and its potassium salt (Biltz and Max), A., i, 591.

Methylfructoside, preparation of, and its derivatives (Irvine and Robertson), A., i, 79.

α-Methylgalactoside, biochemical synthesis of (Aubry), A., i, 72.

Methylgingerol, preparation and properties of (Lapworth, Pearson, and Royle), T., 779; A., i, 571.

β-Methyl glucoside, synthesis of, law of mass action in relation to (Bailly), A., ii, 457.

ε-Methyl-$\Delta^{\alpha\epsilon}$-heptadien-δ-ol, (Enklaar), A., i, 111.

ε-Methylheptan-β-one (*amylacetone*) (Rupe and Wild), A., i, 538.

ε-Methylheptan-δ-one-γε-dicarboxylic acid, ethyl ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 147.

ε-Methyl-$\Delta^{\alpha\gamma\epsilon}$-heptatriene (Enklaar), A., i, 111.

ε-Methylheptoic acid, and its derivatives (Levene and Allen), A., i, 4.

ζ-Methylheptyl alcohol, and its derivatives (Levene and Allen), A., i, 4.

1-Methylhexahydrocarbazole, and its derivatives (v. Braun, Heider, and Neumann), A., i, 168.

δ-Methylhexan-γ-one-βδ-dicarboxylic acid, ethyl ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 147.

δ-Methylhexoic acid, preparation and derivatives of (Levene and Allen), A., i, 3.

ε-Methylhexyl alcohol, and its derivatives (Levene and Allen), A., i, 3.

Methyl hexyl ketone, condensation of pyrrole with (Tschelincev and Tronov), A., i, 412.

1-Methylhydantoylethylamide, 5-hydroxy- (Biltz and Max), A., i, 591.

1-Methylhydrindene, and 2-amino-, and its derivatives (v. Braun, Danziger, and Koehler), A., i, 260.

2-Methylhydrindene, 2-amino-, acetyl derivative, amino-, hydroxy-, and nitro-derivatives of (v. Braun and Danziger), A., i, 263.
  2-amino-, 2-chloro-, 2-hydroxy-, and their derivatives (v. Braun, Kruber, and Danziger), A., i, 131.

1-Methylhydrindene-2-carboxylic acid, ethyl ester (v. Braun, Danziger, and Koehler), A., i, 261.

1-Methyl-2-hydrindylmethyl alcohol (v. Braun, Danziger, and Koehler), A., i, 261.

2-Methyl-2-hydrindylphenylthiocarbamide (v. Braun, Kruber, and Danziger), A., i, 132.

Methyliminobenzoylacetic acid, phenyl ester (Knust and Mumm), A., i, 415.

Methyliminobenzoylacetylmalonic acid, ethyl ester (Knust and Mumm), A., i, 415.

2-Methylindene (v. Braun, Kruber, and Danziger), A., i, 132.

β-2-Methylindolylacrylic acid, α-amino-, benzoyl derivative, and its azlactone (Barger and Ewins), A., i, 477.

3-Methylindone, and its semicarbazone, and 2:6(?)-*di*bromo- (Stoermer and Laage), A., i, 654.

Methylketencarboxylic acid, methyl ester, dimeric (Schroeter, Kesseler, Liesche, and Müller), A., i, 149.

Methylmalonanilic acid, methyl ester (Schroeter, Kesseler, Liesche, and Müller), A., i, 149.

5-Methyl-4-α-methoxyethyl-6-pyrimidone, 2-thio- (Johnson and Hadley), A., i, 667.

1-Methylnipecotinic acid, and its derivatives (Hess and Leibbrandt), A., i, 354.

η-Methylnonane-βδ-dione (*acetylamylacetone*) (Rupe and Wild), A., i, 539.

η-Methylnonoic acid (Levene and Allen), A., i, 4.

Methyl nonyl ketone, preparation of, from palm kernel oil (Salway), T., 407; A., i, 438.

ε-Methyl-$\Delta^{\alpha\epsilon}$-octadien-δ-ol (Enklaar), A., i, 112.

ε-Methyl-$\Delta^{\alpha\gamma\epsilon}$-octatriene (Enklaar), A., i, 112.

ζ-Methyloctoic acid, and its derivatives (Levene and Allen), A., i, 3.

η-Methyloctyl alcohol, and its derivatives (Levene and Allen), A., i, 3.

Methyl-orange, chromoisomerism of (Dehn and McBride), A., i, 594.
  solubilities of, and its salts (Dehn), A., i, 594.

4-Methyl*iso*oxazole-5-one-3-α-propionhydroxamic acid (Schroeter, Kesseler, Liesche, and Müller), A., i, 147.
2-Methylpentamethylene sulphide, and its derivatives (Grischkevitsch-Trochimovski and Cykina), A., i, 156.
β-Methyl-Δ^{α}-penten-γ-one, and its semicarbazone (Mannich), A., i, 635.
γ-Methylpentoic acid, and its derivatives (Levene and Allen), A., i, 4.
Methylphenoxyacetic acids, amino-, bromoamino-, and nitro-, and their derivatives (Jacobs and Heidelberger), A., i, 695.
2-Methylphenylcarbamide. See *o*-Tolylcarbamide.
1-Methylpipecolinic acid, ethyl ester (Hess and Leibbrandt), A., i, 354.
1-Methylpiperidine-2-carboxylic acid. See 1-Methylpipecolinic acid.
1-Methylpiperidine-3-carboxylic acid. See 1-Methylnipecotinic acid.
α-1-Methylpiperidyl-2-propan-β-ol, salts of (Hess, Uibrig, and Eichel), A., i, 351.
α-1-Methylpiperidyl-2-propan-β-one, and its derivatives (Hess, Eichel, and Uibrig), A., i, 352.
Methylpropylacetophenone, and its oxime (Dumesnil), A., i, 654.
Methyl *iso*propyl ketone, condensation of benzaldehyde with (H. and P. Ryan), A., i, 348.
Methyl*iso*propylphenoxyacetic acids, 4-amino-, and their derivatives (Jacobs and Heidelberger), A., i, 696.
4-Methylpyrazole-5-one-3-α propionhydrazide (Schroeter, Kesseler, Liesche, and Müller), A., i, 147.
1-Methylpyrrole-2:5-dicarboxylic acid, and 3:4-*di*bromo-, methyl esters (Tschelincev and Maksorov), A., i, 165.
α-1-Methyl-2-pyrrolidylbutyl alcohol, and its salts (Hess, Uibrig, and Eichel), A., i, 351.
1-Methyl-2-pyrrolidyl propyl ketone, derivatives of (Hess, Eichel, and Uibrig), A., i, 353.
Methylpsychotrine, and its salts and derivatives (Pyman), T., 431; A., i, 410.
2-Methyl-1:4-pyrone, 3-hydroxy-. See Maltol.
1-Methylquinolone, 3:6:8-*tri*nitro- (Kaufmann and de Petherd), A., i, 355.
Methyl-red, use of, as indicator (Lehmann and Wolff), A., ii, 326.
Methylsalicylaldehydes, and their derivatives (Anselmino), A., i, 342.
o-**Methylstyrene** (v. Auwers), A., i, 268.
α-Methylstyrene, 3-hydroxy-, and its acetate (v. Auwers), A., i, 268.
Methyltetrahydrocryptopine (Perkin), A., i, 280.
2- and **3-Methyltetrahydrothiophen**, preparation and derivatives of (Grischkevitsch-Trochimovski and Nekritsch), A., i, 155.
Methylthalline. See 6-Methoxy-1-methyl-1:2:3:4-tetrahydroquinoline.
4-Methylthiazoline, 2-amino-, and 2-thiol-, and their salts (Gabriel and Ohle), A., i, 564.
Methylthiolcarbonic acid, imino-, ethyl ester, derivatives of (Knorr), A., i, 547.
3-Methylthiol-*p*-cresol (Zincke and Arnold), A., i, 264.
Methylthioluramil (Biilmann and Bjerrum), A., i, 178.
Methylthioxanthone, amino-, and chloro- (Ullmann and v. Glenck), A., i, 159.
4-Methylthioxanthone-2:1-acridone (Ullmann and v. Glenck), A., i, 160.
4-Methylthioxanthonyl-1-anthranilic acid (Ullmann and v. Glenck), A., i, 161.
4-Methylthioxanthonyl-1-hydrazine, anhydride of (Ullmann and v. Glenck), A., i, 160.
o-**4-Methylthioxanthonylthiolbenzoic acid** (Ullmann and v. Glenck), A., i, 161.
2-Methyltrimethylene sulphide, and its derivatives (Grischkevitsch-Trochimovski), A., i, 154.
r-**2-Methyltryptophan** (Barger and Ewins), A., i, 477.
Methyluric acids, isomeric (Biilmann and Bjerrum), A., i, 177, 588.
9-Methyluric acid, and its derivatives (Biltz and Heyn), A., i, 291.
α-, ζ- and **δ-Methyluric acids** (Biltz and Heyn), A., i, 292.
1-Methyl-ψ-uric acid, 5-chloro- (Biltz and Strufe), A., i, 294.
Methylzingerone, and its oxime (Nomura), T., 772; A., i, 570; (Lapworth, Pearson, and Royle), T., 786; A., i, 571.
Mice, white, influence of tethelin on growth of (Robertson and Delprat), A., i, 673.
Micro-organisms, effect of carbohydrates on accumulation of ammonia by (Waksman), A., i, 613.
Milk, cryoscopy and refractometry of (Pritzker), A., ii, 549.
  relation of proteins in diet to the production of (Hart, Humphrey, and Surr), A., i, 608.

Milk, influence of coagulation on the gastric digestion of proteins of (Leary and Sheib), A., i, 184.
  distribution of fatty acids in the fat of (Crowther and Hynd), A., i, 608.
  efficiency of substitutes for, in feeding calves (Carr, Spitzer, Caldwell, and Anderson), A., i, 192.
  cow's, influence of parturition on the composition of (Eckles and Palmer), A., i, 68.
    adenine and guanine in (Voegtlin and Sherwin), A., i, 366.
  changes produced by addition of calcium hydroxide to (Bosworth and Bowditch), A., i, 184.
  phosphatides in (Osborne and Wakeman), A., i, 103.
  alcohol test for (Kolthoff), A., ii, 111.
  new indicator for use with (Clark and Lubs), A., ii, 499.
  detection of water in, by the freezing-point method (Polak), A., ii, 279.
  estimation of calcium in (Lyman), A., ii, 271.
  estimation of water in (Keister), A., ii, 550.
Millon's base, luminescence of the iodide of (Weiser), A., ii, 174.
Miloschite from America (Wherry and Brown), A., ii, 148.
Mimetite, hydroxy- (McDonnell and Smith), A., ii, 314.
Minasragrite (Schaller), A., ii, 575.
Minerals from the island of Borneo (Tschernik), A., ii, 484.
  rare Californian (Rogers), A., ii, 496.
  of Candoglia, Italy (Tacconi), A., ii, 495.
  from the Caucasus (Timoféev), A., ii, 495.
  from Graves Mountain, Georgia (T. L. and J. W. Watson), A., ii, 493.
  from Grisons, Switzerland (Müller), A., ii, 149.
  from the Kyshtymsk Mountains (Nikolaev), A., ii, 487.
  from Monte Arco, Elba (Manasse), A., ii, 485.
  Portuguese, containing uranium and zirconium, spectra of (Pereira-Forjaz), A., ii, 113.
  Venetian (Billows), A., ii, 492.
  in the Worthington Mine, Sudbury, Ontario (Walker), A., ii, 486.
  of the mica group, constitution of (W. and D. Asch), A., ii, 494.
  organic origin of (Samoilov), A., ii, 376.
  coloured, ultra-violet transparency of (Absalom), A., ii, 283.
Minerals, red-violet, neodymium in (Wherry), A., ii, 209.
  carbonates, refractive indices of (Gaubert), A., ii, 144.
  silicates, extraction of aluminium and potassium salts from (Frazer, Holland, and Miller), A., ii, 570.
Mineralogy, Chinese, history of (Holgen), A., ii, 326.
Minium from the Tyrol (Dittler), A., ii, 144.
Mixtures (Michaud), A., ii, 122.
  cooling curves of (Parravano and Mazzetti), A., ii, 292.
Molasses, pigments of (Stoltzenberg), A., i, 153 ; (Stanek), A., i, 381.
  nitrogenous pigments of (Friedrich), A., i, 544 ; (Stanek), A., i, 545.
  estimation of raffinose and sucrose in (Staněk), A., ii, 342.
Molecular attraction (Mills), A., ii, 165, 356.
  compounds, organic (Giua), A., i, 386.
  refractivity of nitro-derivatives of alkyltoluidines (Jansen), A., i, 128.
  volumes. See Volumes.
Molecules, existence of (Pihlblad), A., ii, 557.
Molybdenite, electrical properties of (Waterman), A., ii, 162.
Molybdenum, recovery of, from residues (Lenher and Schultz), A., ii, 416.
Molybdenum oxides, action of metaphosphoric acid on (Colani), A., ii, 479.
  sulphides (Mawrov and Nikolov), A., ii, 479.
  Molybdic acid, recovery of (Rudnick and Cooke), A., ii, 320 ; (Kinder), A., ii, 321.
  Molybdates, constitution of (Rosenheim, Pieck, and Pinsker), A., ii, 35.
Molybdenum, estimation of (Weiser), A., ii, 105.
  estimation of, by potassium iodide (Jamieson), A., ii, 275.
  estimation of, in steel (Travers), A., ii, 515.
Montanol, and its acetyl derivative (Grün and Ulbrich), A., i, 5.
Montmorillonite, crystalline (Leitmeier), A., ii, 494.
Morphine, constitution of (Faltis), A., i, 411.
  methyl derivatives of (Mannich), A., i, 473.
  in crude opium (Carles), A., i, 163.
  tolerance to (Biberfeld), A., i, 106.
  estimation of, colorimetrically (Heiduschka and Faul), A., ii, 554.
  estimation of, volumetrically (Rakshit), A., ii, 553.

*apo***Morphine**, constitution and derivatives of (v. Braun and Aust), A., i, 281.

Morphine alkaloids (v. Braun and Kindler), A., i, 163; (v. Braun and Aust), A., i, 281.
  preparation of derivatives of (Soc. Chem. Ind. in Basle), A., i, 664.

Moulds, formation of starch-like substances by (Boas), A., i, 503.
  formation of starch by (Boas), A., i, 370.
  nitrogenous nutrition of (Ehrlich), A., i, 309.

Mountain sickness (Rippstein), A., i, 428.

Mucic acid, equilibrium of, and its lactones (Taylor and Acree), A., ii, 133.
  azide and hydrazide of, and their derivatives (Curtius and Darapsky), A., i, 638.
  p-nitrobenzyl ester (Lyons and Reid), A., i, 559.

Muscle, rabbits', influence of arginine on the creatine content of (Thompson), A., i, 369.
  estimation of dextrose in (Hoagland), A., ii, 515.

Muscovite, action of ammonium sulphate solutions on (Gardiner and Shorey), A., i, 621.

Muscular tissues. See Tissues.

Myristo-*p*-ethoxyanilide (de' Conno), A., i, 388.

Myristo-*p*-hydroxyanilide (de' Conno), A., i, 387.

Myristo-*p*-methoxyanilide (de' Conno), A., i, 388.

Myristo-α- and -β-naphthalides (de' Conno), A., i, 388.

Myristo-*p*-phenylenediamide (de' Conno), A., i, 388.

Myristo-*p*-toluidide (de' Conno), A., i, 387.

Myristo-*m*-xylidide (de' Conno), A., i, 387.

N.

Nagana, effect of arsenic and antimony compounds on (Teichmann), A., i, 527.

Naphtha, adsorption of the solid paraffins of (Rakuzin), A., i, 109.
  solvent, cracking of (Egloff and Moore), A., i, 385.
  estimation of xylene in (Spielmann and Jones), A., ii, 339.

α-Naphthachromanone. See 2:3-Dihydro-α-naphtha-γ-pyrone.

α-Naphthachromone. See α-Naphtha-γ-pyrone.

2:5-Naphthadiazine, 1:3:10-*tri*hydroxy-, and its salts and derivatives (v. Niementowski and Sucharda), A., i, 478.

Naphthafluoran, 3:11-*di*hydroxy-, and its derivatives (Fischer and König), A., i, 661.

Naphthalene, estimation of, in coal gas (Knublauch), A., ii, 427.

Naphthalene, 2- and 4-amino-1:5-*di*hydroxy-, and their salts (Fischer and Bauer), A., i, 694.
  *di*hydroxy-derivatives, carboxylic acids from, and their salts (v. Hemmelmayr), A., i, 646.
  1:6-*di*hydroxy-, action of phthalic anhydride on (Fischer and König), A., i, 661.

Naphthalene-3-carboxylic acid, 2-hydroxy-, preparation of arylamides of (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 271.

Naphthalenedicarboxylic acid, 1:5-*di*hydroxy-, preparation of (v. Hemmelmayr), A., i, 457.

α-Naphtha-γ-pyrone, preparation of, and its semicarbazone (Pfeiffer and Grimmer), A., i, 662.

α-Naphtha-γ-pyrone-2-carboxylic acid, ethyl ester (Pfeiffer and Grimmer), A., i, 662.

2(1:4)-Naphthaquinonyl-1′-naphthylsulphone (Hinsberg), A., i, 576.

2(1:4)-Naphthaquinonylphenylsulphone, 3-hydroxy- (Hinsberg), A., i, 576.

1:8-Naphthasultam, 4-amino-, *mono*- and *di*-chlorohydroxy-, 4-hydroxy-, and 3:4-*di*hydroxy-, and their derivatives (Zincke and Schürmann), A., i, 38.

1:8-Naphthasultam-3:4-phenazine, and 2-chloro-, and 2-hydroxy-, and their derivatives (Zincke and Schürmann), A., i, 39.

1.8-Naphthasultam-4-quinone, and 2-*mono*-, 2:3-*di*-, and 2:2:3:3-*tetra*-chloro-, 2-chloro-3-hydroxy-, and 3-hydroxy-, and their derivatives (Zincke and Schürmann), A., i, 38.

Naphthenes, action of sulphur on (Friedmann), A., i, 13.

Naphthindazine-9-sulphonic acid (Kehrmann and Herzbaum), A., i, 592.

Naphthoic acid, β-hydroxy-, *p*-nitrobenzyl ester (Lyons and Reid), A., i, 559.

α- and **β-Naphthols**, crystallography of (Stortenbeker; Steinmetz), A., i, 557.
  differentiation between (Denigès), A., ii, 48.
  detection of (Guglialmelli), A., ii, 547

α- and β-**Naphtholphenolphthaleins,** and their acetates (Orndorff and Murray), A., i, 339.

Naphtholphthalein, use of, in colorimetric analysis (Moir), A., ii, 386.

α-**Naphthol-3-sulphonic acid,** 6-amino-, preparation of acyl derivatives of (Chemische Fabrik Griesheim Elektron), A., i, 453.

Naphth*iso*oxadiazole, and its oxide, preparation of (Green and Rowe), T., 616; A., i, 518.

1-Naphthoxyacetic acid, 4-amino-, and its acetyl derivative (Jacobs and Heidelberger), A., i, 697.

o-**2-Naphthoylbenzoic acid,** 1:6-*di*hydroxy- (Fischer and König), A., i, 661.

β-**2-Naphthoylpropionic acid,** methyl ester (Giua), A., i, 394.

Naphthyl ethers, action of oxalyl chloride on (Giua), A., i, 204.

  sulphites (Richter), A., i, 24.

Naphthylacetic acids, ethyl esters (Wislicenus and Elvert), A., i, 202.

Naphthylamines, bromo- (Franzen and Åaslund), A., i, 644.

Naphthylglyoxylic acid, hydroxy-, lactone of (Giua), A., i, 205.

3-β-Naphthyl-5-*op*-*di*hydroxybenzylidenerhodanine (Andreasch), A., i, 663.

β-**Naphthylhydroxylamine,** and its salts and β-nitroso- (Baudisch and Fürst), A., i, 330.

1-β-Naphthyl*iso*indazole, 4-bromo-, and 4-chloro- (Reich and Turkus), A., i, 585.

2-Naphthyl β-*p*-methoxyphenylethyl ketone, 1-hydroxy- (Pfeiffer and Grimmer), A., i, 663.

2-Naphthyl *p*-methoxystyryl ketone, 1-hydroxy- (Pfeiffer and Grimmer), A., i, 662.

2-Naphthylphenylsulphone, 1:4-*di*hydroxy- (Hinsberg), A., i, 576.

2-Naphthylquinoline-4-carboxylic acids (Chemische Fabrik auf Aktien vorm. E. Schering), A., i, 96.

Narcosis (Höber; Winterstein), A., i, 68.

Narcotics, detection of (Hankin), A., ii, 184.

Narcotine, compound of mercuric nitrite and (Rây), T., 508; A., i, 470.

Natrojarosite from Kundip, Western Australia (Simpson and Brown), A., ii, 146.

Neodymium in red-violet minerals (Wherry), A., ii, 209.

  diphenylsulphonate and ferricyanide (Grant and James), A., ii, 316.

Neomolybdenum (Gerber), A., ii, 575.

Neon, spectrum of (Meissner), A., ii, 61.

  critical constants of (Onnes, Crommelin, and Cath), A., ii, 407.

  dilatability and internal pressure of (Leduc), A., ii, 356.

Neotungsten (Gerber), A., ii, 575.

Nephelites (Bowen), A., ii, 178.

Nephelometer-colorimeter (Kober), A., ii, 266.

Nephritis, diastatic activity of blood in (Myers and Killian), A., i, 369.

Nereocystis luetkeana (kelp), carbon monoxide in (Langdon), A., i, 372.

Nernst's formula, application of, to homologous series (Herz), A., ii, 441.

Nervous system, central, proteins of (McGregor), A., i, 185.

Neurokeratin, composition of (Nelson), A., i, 61.

Nichrome, analysis of (Reid), A., ii, 392.

Nickel alloys resistant to sulphuric acid (Irmann), A., ii, 478.

  with chromium and iron, analysis of (Reid), A., ii, 392.

  with iron, expansion of (Guillaume), A., ii, 356.

  with zirconium, analysis of (Kelley and Myers), A., ii, 544.

Nickel azide (Wöhler and Martin), A., i, 383.

  selenates (Tutton), A., ii, 415.

Nickel detection, estimation, and separation:—

  detection and estimation of (Grossmann and Mannheim), A., ii, 391.

  estimation of, in presence of iron and zinc (Rothschild), A., ii, 221.

  estimation of, in ores and alloys (Schoeller and Powell), A., ii, 425.

  estimation of, in iron ores (Covitz), A., ii, 153.

  separation of copper and (Grossmann and Mannheim), A., ii, 512.

Nickel steel (Dejean), A., ii, 477.

Nicotine, distillation of, in steam (Brezina), A., ii, 348.

  compound of mercuric nitrite and (Rây), T., 507; A., i, 470.

  estimation of, in tobacco (Tingle and Ferguson), A., ii, 55; (Thomsen), A., ii, 431.

Ninhydrin reaction (Retinger), A., i, 519.

Niton (*radium emanation*), rate of diffusion and diameter of the atom of (Róna), A., ii, 286.

  removal of, from water, by the bubbling method (Moran), A., ii, 63.

Nitric acid. See under Nitrogen.

Nitrification in soils (Kelley), A., i, 431; (Gainey and Metzler; Münter), A., i, 722.

effect of paraffin on (Gainey), A., i, 721.

effect of alkali salts on (Brown and Hitchcock), A., i, 717.

and ammonification in soils (Lipman and Burgess), A., i, 243; (Miyake), A., i, 244.

Nitriles, preparation of (van Epps and Reid; Stähler), A., i, 13.

preparation of, from aliphatic amines (Mailhe and de Godon), A., i, 686.

formation of, from amines (Sabatier and Gaudion), A., ii, 460.

hydrolysis of, by hydrogen peroxide (McMaster and Langreck), A., i, 334.

unsaturated, condensation of phloroglucinol with (Fischer and Nouri), A., i, 469.

detection of (Dezani), A., ii, 549.

Nitroamines, estimation of nitrogen in (Cope and Barab), A., ii, 40.

o-**Nitroamines**, conversion of, into *iso*-oxadiazole oxides (Green and Rowe), T., 612; A., i, 518.

Nitro-compounds, preparation of (Heinemann), A., i, 126.

reduction of (Jacobs and Heidelberger), A., i, 559; (Cusmano), A., i, 641.

aromatic (Giua), A., i, 18.

toxicity of (Koelsch), A., i, 716.

estimation of nitrogen in (Sachs), A., ii, 505.

Nitrogen, distance between atoms in the molecule of (Silberstein), A., ii, 161.

active, spectrum of (Strutt), A., ii, 282.

quinquevalent, stereochemistry of (Komatsu), A., i, 139.

combination of carbon with (Lidov), A., ii, 86.

sources of, for yeasts and moulds (Ehrlich), A., i, 309.

distribution of, in beer (Sharpe), A., i, 620.

amino-acid, in blood (Bock), A., i, 360.

non-protein, in blood of fresh-water fish (Wilson and Adolph), A., i, 360.

Nitrogen compounds, molecular refractivities of (Le Bas), A., ii, 349.

analogy between oxygen compounds and (Angeli), A., i, 452.

Nitrogen *tri*chloride, preparation and reactions of (Dowell and Bray), A., ii, 306.

Nitrogen *di*oxide (*nitric oxide*), action of, on metallic peroxides (Dutt and Sen), A., ii, 85.

oxides, estimation of, in air (Usher and Rao), T., 799; A., ii, 502.

Nitric acid, optical investigations of the constitution of (Schaefer and Niggemann), A., ii, 61.

formation of, by oxidation of ammonia (Maxted), A., ii, 465.

absorption spectrum of the vapour of (Schaefer and Deichsel), A., ii, 186.

optical investigations of mixtures of sulphuric acid and (Schaefer and Niggemann), A., ii, 186.

distillation of mixtures of sulphuric acid, water and (Pascal), A., ii, 569.

removal of, from solutions of organic compounds (Levene and Meyer), A., ii, 530.

estimation of, colorimetrically (Smith), A., ii, 217.

estimation of, in presence of picric and sulphuric acids (Richardson), A., ii, 158.

Nitrates, isomorphism of chlorates and (Rea), A., i, 633.

formation of double sulphates and (Massink), A., ii, 412.

assimilation of (Baudisch), A., i, 434; (Loew), A., i, 615.

detection of, purification of sulphuric acid for use in (Steenbergen), A., ii, 421.

estimation of, in presence of chlorides (Gericke), A., ii, 421.

estimation of, in sewage (Phelps and Shoub), A., ii, 504.

estimation of, in soils (Davis), A., ii, 329.

estimation of, in water (Nichols), A., ii, 421.

estimation of nitrogen in (Arnd), A., ii, 504.

Nitrous acid, velocity of decomposition and dissociation constant of (Rây, Dey, and Ghosh), T., 413; A., ii, 301.

action of, on lysine (Sure and Hart), A., ii, 551.

action of, on urea (Werner), T., 863; A., i, 639.

Nitrites, assimilation of (Baudisch), A., i, 434.

precipitation of (Hahn), A., ii, 382.

estimation of nitrogen in (Arnd), A., ii, 504.

Nitrogen organic compounds, asymmetric quinquevalent, preparation of (Meldola, Foster, and Brightman), T., 533, 546, 551; A., i, 453, 454.
  resolution of (Reilly), T., 20; A., i, 129.
Nitrogen estimation:—
  estimation of (Kahn), A., ii, 100; (Salkowski), A., ii, 504.
  estimation of, by Kjeldahl's method (Kober), A., ii, 40; (Wolf-Joachimowitz), A., ii, 217; (Abderhalden and Fodor), A., ii, 540; (Nolte), A., ii, 578.
  estimation of, in mixed gases (Brandt), A., ii, 384.
  estimation of, in manures (Lagers), A., ii, 329.
  estimation of, in mercury organic compounds (Justin-Mueller), A., ii, 39.
  estimation of, in nitrates and nitrites (Arnd), A., ii, 504.
  estimation of, in nitroamines (Cope and Barab), A., ii, 40.
  estimation of, in nitro-compounds (Sachs), A., ii, 505.
  estimation of, in soils (Latshaw), A., ii, 100.
  estimation of, in urine (Ljungdahl), A., ii, 578.
  estimation of, in urine, by means of potassium persulphate (Scott and Myers), A., ii, 380.
  amino-, estimation of, in blood (Bock), A., ii, 159.
    estimation of, in urine (van Slyke), A., ii, 41.
  metabolic, estimation of, in fæces (Forbes, Mangels, and Morgan), A., i, 524.
  nitric, estimation of (Scales), A., ii, 41.
    estimation of, in soils (Greaves and Hirst), A., ii, 578.
Nitrolime, estimation of dicyanodiamide in (Stutzer), A., ii, 159; (Hager and Kern), A., ii, 518.
"**Nitron**," use of, in analysis of substances used in explosives (Cope and Barab), A., ii, 268.
Nitrosoamines, refractivity of (Jansen), A., ii, 401.
  action of, on hydrazines (Fischer and Chur), A., i, 708.
o-**Nitrosoamines**, conversion of, into *iso*oxadiazoles (Green and Rowe), T., 612; A., i, 518.
Nitroso-compounds, reduction of (Cusmano), A., i, 641.
Nitrosyl chloride, dissociation equilibrium of (Trautz and Hinck; Trautz and Wachenheim), A., ii, 74.
Nitrous acid. See under Nitrogen.
Nitrous air, antiseptic properties of (Colin), A., ii, 466.
Nivalic acid (Hesse), A., i, 458.
Nomon, a device for chemical calculations (Deming), A., ii, 567.
Nonaldehyde, constants and derivatives of (Harries and Oppenheim), A., i, 211.
Non-electrolytes, influence of salts on the solubility of (v. Euler and Svanberg), A., ii, 445.
Nopinone, derivatives of (Harries and v. Splawa-Neyman), A., i, 213.
*iso***Nortropinone** (Houben and Pfau), A., i, 25, 162.
Nucleic acids, rotation of, and of their alkali salts (Rakuzin and Braudo), A., i, 99.
β-**Nucleoproteins**, antigenic properties of (Wells), A., i, 98.
Nutrition of green plants (Bokorny), A., i, 718.
Nux vomica, estimation of strychnine in (Jensen), A., ii, 56.

O.

Oak bark, rotten, constituents of (Sullivan), A., i, 8.
Oats, effect of, on growth and development (McCollum, Simmonds, and Pitz), A., i, 185.
  changes in urea in blood and tissues due to diet of (Lewis and Karr), A., i, 100.
Obituary notices:—
  Andrea Angel, T., 321.
  Frederick William Caton, T., 312.
  Edward Davies, T., 323.
  Heinrich Debus, T., 325.
  William Esson, T., 332.
  Charles George Edgar Farmer, T., 314.
  John Ferguson, T., 333.
  John Griffiths, T., 315.
  David Howard, T., 342.
  Leonard de Koningh, T., 348.
  Ernest Alfred Lewis, T., 348.
  James McConnan, T., 316.
  Cyril Douglas McCourt, T., 318.
  Raphael Meldola, T., 349.
  Hugo Müller, T., 572.
  Raymond William Nichols, T., 319.
  Thomas Purdie, T., 359.
  Sir William Ramsay, T., 369.

Obituary notices :—
William Gilbert Saunders, T., 320.
Frederick Wallis Stoddart, T., 376.
Edwin Whitfield Wheelwright, T., 377.
John Wrightson, T., 378.
Oceanic salts, solutions of (Jänecke), A., ii, 527.
Ocotea usambarensis, ψ-cubebin in (Halberkann), A., i, 507.
Octaldehyde, derivatives of (Harries and Oppenheim), A., i, 211.
Odour, relation between chemical constitution and (Prins), A., i, 607.
adsorption of (van Dam; Kremer), A., i, 607.
specific intensity of (Zwaardemaker), A., ii, 63.
Oils, fractionation of (Seidenberg), A., i, 626.
aromatic, cracking of (Egloff and Moore), A., i, 385.
light, analysis of (Egloff), A., ii, 338.
essential. See Oils, vegetable.
vegetable, influence of climatic conditions on (Pigulevski), A., i, 189.
obtained from spruce cellulose (Kertész), A., i, 8.
detection of phenols in (Guglialmelli), A., ii, 514.
analysis of (Lecoq), A., ii, 399.
estimation of unsaponifiable matter in (Davidsohn), A., ii, 183; (Wilkie), A., ii, 429.
separation of cholesterol and phytosterol from (Prescher), A., ii, 275, 514.
Oilsylvic acid (Schulz), A., i, 649.
Oleic acid, compound of aluminium chloride and (Gangloff and Henderson), A., i, 533.
preparation of esters of, and their reduction products (Ellis and Rabinovitz), A., i, 78.
effect of bile on the reaction between sodium hydrogen carbonate and (Kingsbury), A., i, 362.
Oleoanilide (de' Conno), A., i, 387.
Oleo-*p*-ethoxyanilide (de' Conno), A., i, 388.
Oleo-*p*-hydroxyanilide (de' Conno), A., i, 388.
Oleo-*p*-methoxyanilide (de' Conno), A., i, 388.
Oleo-α- and -β-naphthalides (de' Conno), A., i, 388.
Oleo-*p*-phenylenediamide (de' Conno), A., i, 389.
Oleo-*p*-toluidide (de' Conno), A., i, 387.
Oleo-*m*-xylidide (de' Conno), A., i 387.
Olfactology of aromatic hydrocarbons (Backman), A., i, 498.
Olfactometer, new (van Dam), A., i, 606.
Olivetoric acid, derivatives of (Hesse), A., i, 457.
Olivetorinol (Hesse), A., i, 457.
Olivoric acid, and its potassium salt (Hesse), A., i, 457.
*apo***Olivoric acid** (Hesse), A., i, 457.
Opianic acid, and nitro-, action of phenylhydrazine on (Mitter and Sen), T., 988; A., i, 710.
Opium, crude, morphine in (Carles), A., i, 163.
detection of (Tunmann), A., ii, 226.
Opium alkaloids, toxic action of, on paramœcia (Macht and Fisher), A., i, 678.
Optical inversion, Walden's (Senter and Martin), T., 447; A., ii, 301.
Optically active compounds, rotation of (Patterson), A., ii, 3.
chemical constitution and rotation of (Rupe and Wild), A., i, 538; (Rupe and Silberstrom), A., ii, 435.
Ores, estimation of sulphides in (Scheidler), A., ii, 503.
Organic compounds, absorption spectra and chemical constitution of (British Association Reports), A., ii, 435.
relation between thermal properties and constitution of (Pagliani), A., ii, 120.
relation between constitution and coagulating capacity of (Gann), A., ii, 21.
homologous, physical properties of (Herz), A., ii, 236.
application of Guldberg and Trouton-Nernst rules to (Herz), A., ii, 441.
coloured additive (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 205.
combustion of, and chemical affinity (Thornton), A., ii, 357.
oxygen and heat required for combustion of (Thornton), A., ii, 164.
action of ozone on (Harries), A., i, 210.
preparation of chloro-derivatives of (Société Chimique des Usines du Rhône), A., i, 15.
catalytic hydrogenation of (Badische Anilin- & Soda-Fabrik), A., i, 377.
aromatic, action of aromatic alcohols with, in presence of aluminium chloride (Huston and Friedemann), A., i, 19.

Organic compounds, aromatic, halogenated, condensations of (Meyer and Hofmann), A., i, 641.
  as nutriment for green plants (Bokorny), A., i, 718.
  micro-analysis of (Wise), A., ii, 541.
  estimation of arsenic in (Ewins), A., ii, 101.
  estimation of bromine and of sulphur in (Merl and Lüft), A., ii, 383.
  estimation of chlorine in (Lemp and Broderson), A., ii, 539.
  estimation of halogens in (Kelber), A., ii, 215.
  estimation of mercury in (Marsh and Lye), A., ii, 219; (Lomholt and Christiansen), A., ii, 424.
  estimation of silver in (Lucas and Kemp), A., ii, 542.
Organism, animal, behaviour of hydroaromatic substances in the (Sasaki), A., i, 677.
Organisms, marine, composition of sea-water to keep alive (McClendon), A., i, 105.
Organs, animal, method of drying (Wiechowski), A., i, 520.
Ornithine, γ-hydroxy-, α-benzoyl derivative, and its salts (Hammarsten), A., i, 82.
Ortstein, formation of, in soils (Stremme), A., i, 512.
Osmium, action of selenic acid on (Hradecky), A., ii, 483.
Osmium *di*oxide, preparation and properties of (Ruff and Rathsburg), A., ii, 323.
Osmosis (Hamburger), A., ii, 562.
  with semi-permeable membranes (Bancroft), A., ii, 444.
Osmotic pressure (Tinker), A., ii, 294.
  nature and origin of (Horiba), A., ii, 410.
  of colloids (Biltz, Bugge, and Mehler), A., ii, 17.
Osmotic theory of solutions (Jellinek), A., ii, 294.
Ovalbumin. See Albumin.
Overvoltage (Newbery), T., 470; A., ii, 290, 355.
  tables of (Newbery), A., ii, 12, 64.
*iso***Oxadiazoles**, conversion of *o*-nitrosoamines into (Green and Rowe), T., 612; A., i, 518.
*iso***Oxadiazole** oxides, conversion of *o*-nitroamines into (Green and Rowe), T., 612; A., i, 518.
Oxalic acid, kinetics of oxidation of, and its salts (Dhar), T., 707; A., ii, 458.
  alkali salts, solubility of, in presence of alkali salts (Colani), A., i, 78.
Oxalic acid, alkaline earth salts of (Œchsner de Coninck), A., i, 194.
  alkaline earth hydrogen salts of (Bruhns), A., i, 534.
  equilibrium of ammonium and uranyl salts of, with water (Colani), A., i, 535.
  equilibrium of the sodium and uranyl salts of, with water (Colani), A., i, 513.
  cerous salt, effect of heating in an inert or reducing atmosphere (Chase), A., ii, 475.
  ethyl ester, compound of potassium iodide and iodine with (Skrabal), A., i, 378.
    condensations with (Wislicenus and Schöllkopf), A., i, 700.
  ethyl and benzyl esters, compounds of thiocarbamide with (Taylor), T., 661; A., i, 514.
  methyl ester, solubility of, in water (Skrabal), A., i, 317.
    hydrolysis of (Skrabal), A., ii, 250.
  phenylhydrazine ester, comparison of mesoxalic acid phenylhydrazone with (Evans, Mong, and Sinks), A., i, 595.
  estimation of alkalis by means of (Bruhns), A., ii, 270.
  detection of, in wines (Besson), A., ii, 516.
  estimation of, in foods (Arbenz), A., ii, 583.
α-**Oxalo**-β-**diphenylenepropionic acid**, diethyl ester, and its potassium derivative (Wislicenus and Eble), A., i, 272.
α-**Oxalo**-γγ-**diphenylpropionic acid**, ethyl ester, isomerism and derivatives of (Wislicenus and Eble), A., i, 271.
Oxalyl chloride, action of, on alcohols (Adams and Weeks), A., i, 4.
    action of, on naphthyl ethers (Giua), A., i, 204.
Oxalylacetoacetic acid, ethyl ester, and its salts and derivatives (Wislicenus and Schöllkopf), A., i, 701.
Oxalyldiaspartic acid, ethyl ester (Bornwater), A., i, 121.
Oxalyldileucylglycinic acid, ethyl ester (Bornwater), A., i, 121.
Oxalyldiphenylalaninic acid, ethyl ester (Bornwater), A., i, 121.
Oxalyldisarcosinic acid, ethyl ester (Bornwater), A., i, 121.
Oxalylhydrazide, estimation of (Datta and Choudhury), A., ii, 108.
Oxanilic acid, *m*- and *p*-amino-, and their derivatives (Jacobs and Heidelberger), A., i, 583.

Oxidation (Dhar), T., 707 ; A., ii, 458.
  without acid (Neidle and Crombie), A., ii, 93.
Oxindole, preparation and derivatives of (Heller and Heine), A., i, 220.
Oxydase, relation of hydrion concentration to activity of (Reed), A., i, 62.
  mechanism of the action of (Reed), A., i, 358, 423.
  action of, in plants (Kastle and Buckner), A., i, 372.
  in plant tissues and juices (Bunzell), A., i, 107.
  relation between catalase and, in plants (Reed), A., i, 424.
Oxygen, distance between atoms in the molecule of (Silberstein), A., ii, 161.
  atomic volume of, at the critical point (Le Bas), A., ii, 193.
  volume ratio of combination of hydrogen with (Guye), A., ii, 412.
  union of hydrogen and, in presence of catalysts (Hofmann and Ebert), A., ii, 25.
  effect of the partial pressure of, on combustion (Dollwig, Kolls, and Loevenhart), A., ii, 569.
  apparatus for registering excess of, in lead-chamber gases (Pérégrin), A., ii, 39.
  dissolved in rain water (Richards), A., i, 624.
Oxygen compounds, molecular refractivities of (Le Bas), A., ii, 349.
  analogy between nitrogen compounds and (Angeli), A., i, 452.
Oxygen, estimation :—
  estimation of, in blood (van Slyke), A., ii, 328.
  estimation of, in water (Bruhns), A., ii, 100.
  estimation of, dissolved in water (Noll), A., ii, 502.
  available, estimation of, in pyrolusite (Barnebey), A., ii, 581.
Oxyhæmoglobin, absorption of light by (Hári), A., i, 597.
  crystals of (Krummacher), A., i, 303.
Ozone, absorption bands of, in the spectra of sun and stars (Fowler and Strutt), A., ii, 522.
  colour and oxidising value of solutions of (Fischer and Tropsch), A., ii, 463.
  action of, on iodine compounds (Riesenfeld and Bencker), A., ii, 201 ; (Harries), A., ii, 464.
  action of, on organic compounds (Harries), A., i, 210.
Ozone, estimation of (David), A., ii, 216.
  estimation of, in air (Usher and Rao), T., 799 ; A., ii, 502.

P.

Paleophysiology (Samoilov), A., ii, 376.
Palladium, melting point of, and Wien's constant C_2 (Holst and Oosterhuis), A., ii, 144.
Palladium cathode. See Cathode.
Palladium organic compounds (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541 ; (Gutbier and Fellner), A., i, 542.
Palm kernel oil, preparation of methyl nonyl ketone from (Salway), T., 407 ; A., i, 438.
Palmitic acid, *p*-nitrobenzyl ester (Lyons and Reid), A., i, 559.
Palmito-*p*-ethoxyanilide (de' Conno), A., i, 388.
Palmito-*p*-hydroxyanilide (de' Conno), A., i, 387.
Palmito-*p*-methoxyanilide (de' Conno), A., i, 388.
Palmito-α- and -β-naphthalides (de' Conno), A., i, 388.
Palmito-*p*-phenylenediamide (de' Conno), A., i, 389.
Palmito-*m*-xylidide (de' Conno), A., i, 387.
Pancreas, glycolytic enzymes of (Lombroso), A., i, 182.
Pancreatin, properties of (Rakuzin and Pekarskaja), A., i, 422.
Pangium edule, seeds of. See Seeds.
Pansy. See *Viola tricolor*.
Papain, proteolytic activity of (Frankel), A., i, 597.
Paradol (Nelson), A., i, 572.
Paramœcia, toxic action of opium alkaloids on (Macht and Fisher), A., i, 678.
Paris green, analysis of (Peters and Fielding), A., ii, 104.
Parmatic acid (Hesse), A., i, 457.
Parmelia saxatilis, constituents of (Ryan and O'Riordan), A., i, 342.
Passivity and overvoltage (Newbery), A., ii, 64.
Pea, garden, nutrition of seedlings of, with calcium and ammonium salts (Morsov), A., i, 616.
Peas, influence of metallic salts on the germination of (Maquenne and Demoussy), A., i, 530.
Peanut. See *Arachis hypogæa*.

- **Pectin** (Schryver and Haynes), A., i, 245.
  - consistency of gels of (McNair), A., i, 80.
- **Pectinogen** (Schryver and Haynes), A., i, 245.
- **Pectin substances** (Ehrlich), A., i, 321; (Odén), A., i, 379, 436.
- **Pelargonenin**, and its chloride (Willstätter and Bolton), A., i, 43.
- **Pellagra**, effect of maize on (Suárez), A., i, 69.
- **Pelletierine**, and its salts and derivatives (Hess), A., i, 349; (Hess and Eichel), A., i, 350.
- **Pentamethylene** sulphide, and its derivatives (Grischkevitsch-Trochimovski and Cykina), A., i, 156.
- **Pentamethylene-oxide-α-carboxylic acid**, γδ-*di*hydroxy-. See Hexahydrocomenic acid.
- **5:7:8:3′:4′-Pentamethoxyflavanone**, and 3-*iso*nitroso- (Nierenstein), T., 9; A., i, 150.
- **Pentamethylorcinol**, derivatives of (Herzig and Wenzel), A., i, 133.
- **Pentane**, γ-*mono*-, and αγ-*di*-bromo- (Rozanov), A., i, 84.
- *iso***Pentane**, β-chloro-, preparation of (Badische Anilin- & Soda-Fabrik), A., i, 77.
- **Pentanes**, thermal and pressure decomposition of (Egloff), A., i, 109.
- **Pentane-βγε-tricarboxylic acid**, β-hydroxy- (Küster and Weller), A., i, 443.
- *cyclo***Pentane-2:4:5-trione-1-carboxylic acid**, ethyl ester, and its salts and derivatives (Wislicenus and Schöllkopf), A., i, 701.
- **Pentosuria**, nature of pentose in (Hiller), A., i, 497.
- **Pepsin**, action of (Ringer), A., i, 233.
  - action of, on trypsin (Long and Hull), A., i, 361, 602.
  - detection of (Graber), A., ii, 60.
- **Peptides**, synthesis of, in the animal organism (Pauly), A., i, 525.
- **Peptisation**, theory of (Bancroft), A., ii, 129.
- **Peptone**, use of alkalis in estimating (Palet), A., ii, 555.
- **Perarsenates.** See under Arsenic.
- **Perborates.** See under Boron.
- **Percarbonates.** See under Carbon.
- **Perchlorates.** See under Chlorine.
- **Perchloric acid.** See under Chlorine.
- **Percrystallisation** (Kober), A., ii, 295.
- **Periodates.** See under Iodine.
- **Periodic law** and overvoltage (Newbery), A., ii, 12.
- **Periodic system** (Silbermann), A., ii, 27.
  - curves of (Thornton), A., ii, 367.
- **Permeability** (Brown and Tinker), A., i, 74; (Brooks), A., i, 371; (Stiles and Jörgensen; Osterhout), A., i, 435.
  - estimation of (Wodehouse), A., i, 371.
- **Permutites**, exchange of bases in (Ramann and Spengel), A., ii, 468.
- **Peroxydase**, nature of (van der Haar), A., i, 301; (Woker), A., i, 485.
  - from plants, action of (Reed), A., i, 424.
- **Perphosphates.** See under Phosphorus.
- **Per-salts**, preparation of (Aschkenasi), A., ii, 467, 468.
- **Perstillation** (Kober), A., ii, 295.
- **Persulphates.** See under Sulphur.
- **Pervaporation** (Kober), A., ii, 295.
- **Petroleum**, adsorption of the paraffin constituents of (Rakuzin), A., i, 109.
  - preparation of aromatic hydrocarbons from (Rittmann), A., i, 14; (Egloff and Twomey), A., i, 110.
  - light, analysis of (Formánek, Knop, and Korber), A., ii, 581.
  - detection and estimation of sulphur in (Francis and Crawford), A., ii, 379.
- **Petunia**, anthocyanin of (Willstätter and Burdick), A., i, 49.
- **Petunidin** and **Petunin**, and their chlorides (Willstätter and Burdick), A., i, 49.
- **Pharmaceutical preparations**, estimation of mercury in (Herrmann), A., ii, 399.
- *Phaseolus vulgaris* (white bean), dietary deficiencies of (McCollum, Simmonds, and Pitz), A., i, 363.
- **Phase rule**, Gibbs' (Viola), A., ii, 81.
- **Phenacetin**, detection of, microchemically (Tunmann), A., ii, 552.
  - estimation of, in presence of salol (Salkover), A., ii, 53.
- **Phenanthraquinone**, additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 207.
- *l*-**Phenanthrene-10:3(or 6)-disulphonic acid**, and its chloride and barium salt (Sandqvist), A., i, 552.
- **Phenazthionium salts**, action of aliphatic amines on (Kehrman, Robert, and Sandoz), A., i, 226.
- *p*-**Phenetidine** hydrochloride, action of formaldehyde on (Lepetit and Maimeri), A., i, 452.

- *p*-**Phenetidinethioindamidine-*p*-phenetidine** (Lepetit), A., i, 198.
- *o*- and *p*-**Phenetidinium** palladochlorides (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.
- *p*-**Phenetidinomethanesulphonic acid**, sodium and *p*-phenetidine salts, and their derivatives (Lepetit), A., i, 197, 198.
- **Phenetole**, 3:5-*di*nitro-2:4-*di*amino- (G. M. and R. Robinson), T., 934.
- **Phenetole-*p*-sulphonic acid**, 2:6-*di*iodo-, and its salts (Rupp and Hermann), A., i, 517.
- **Phenol**, preparation of (J. W. and A. M. Aylsworth, and The Savings, Investments and Trusts Co.), A., i, 331; (Terrisse), A., i, 689.
  - production of, by bacteria (Berthelot), A., i, 305.
  - equilibrium in the system, aniline and (Voano), A., ii, 81.
  - compounds of, with pyridine (Hatcher and Skirrow), A., i, 665.
  - influence of inositol on the excretion of, by dogs (Dubin), A., i, 187.
  - estimation of, in commercial cresylic acid (Fox and Barker), A., ii, 513.
  - estimation of, in mixtures with higher phenols and tar oils (Weiss and Downs), A., ii, 427.
- **Phenol**, amino-, chloroacetyl derivatives of (Jacobs and Heidelberger), A., i, 552.
  - *tri*iodo-, silver salt (Woollett), A., i, 25.
  - 2-iodo-3-nitro-, and 2:4-*di*iodo-6-nitro-, ammonium salts (Datta and Prosad), A., i, 332.
  - *p*-nitro-, as an indicator in water analysis (Goldberg), A., ii, 498.
  - 2:4-*di*nitro-, toxicity and urological action of (Lutz and Baume), A., i, 611.
  - 3:5-*di*nitro- (Steinmetz), A., i, 549.
- **Phenols**, polyhydric, action of alkali hydrogen carbonates on (v. Hemmelmayr), A., i, 645.
  - physiology of (Dubin), A., i, 602.
  - identification of (Reid), A., i, 333.
  - detection of, spectroscopically (Formánek and Knop), A., ii, 513.
  - detection of, in essential oils (Guglialmelli), A., ii, 514.
- **Phenols**, *di*chloro-, preparation and properties of (Holleman), A., i, 556.
- **Phenolanilinephthaleinanilide** (Orndorff and Murray), A., i, 339.
- **Phenol*tetra*chlorophthalein** methyl ether (Orndorff and Murray), A., i, 340.
  - and amino-, bromonitro-, and nitro-, and their derivatives (Orndorff and Rose), A., i, 31.
- **Phenoldiazoniumsulphonates.** See Benzenediazoniumsulphonates, hydroxy-.
- **Phenolglucosides**, synthesis of, and their derivatives (Fischer and v. Mechel), A., i, 216.
- **Phenolresorcinolphthaleins**, and their acetates (Orndorff and Murray), A., i, 339.
- **Phenolsulphonephthalein**, and its derivatives, electrical conductivity of solutions of (White and Acree), A., i, 340.
- **Phenolsulphonic acid**, zinc salt, estimation of, volumetrically (Adanti), A., ii, 517.
- **Phenoxyacetic acids**, amino-, bromoamino-, and their derivatives (Jacobs and Heidelberger), A., i, 625.
- γ-**Phenoxybutyric acids**, *o*- and *p*-amino-, and their derivatives (Jacobs and Heidelberger), A., i, 698.
- **Phenoxypropyl** bromide. See Phenyl γ-bromopropyl ether.
- **Phenyl** γ-bromopropyl ether, amino-, acetyl derivatives (Jacobs and Heidelberger), A., i, 698.
  - *cyclo*hexyl ether (Kursanov), A., i, 398.
  - sulphite, and chloro- and bromo- (Richter), A., i, 24.
- **Phenylacetamide**, amino-, derivatives of (Jacobs and Heidelberger), A., i, 553.
- **Phenylacetic acid**, *p*-nitrobenzyl ester (Lyman and Reid), A., i, 334.
- **Phenylacetic acid**, *p*-amino-, and *p*-nitro-, β-diethylaminoethyl esters, and their salts (Pyman), T., 169; A., i, 304.
  - α-amino-β-3:4-*di*hydroxy- (Bloch), A., i, 675.
  - 2-nitro-4-cyano-, ethyl esters (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 16.
- **Phenylacetoacetic acid**, 2-nitro-4-cyano-, ethyl ester (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 16.
- **Phenylacetonitrile**, 2:6-*di*nitro- (Reich and Oganessian), A., i, 554.
- **Phenylacetonitriles**, nitro-, salts and esters of (Opolski, Kowalski, and Pilewski), A., i, 25.
- **Phenylacetylene**, sodium derivative, condensation of tolylthiocarbimides with (Worrall), A., i, 335.

Phenylacetylhydroxylamide (Bougault), A., i, 695.

Phenylacetylsemicarbazide hydrochloride (Bougault), A., i, 689.

Phenylalaninamide (Bornwater), A., i, 121.

Phenylalanine-carbamido-acid. See *α*-Carbamido-*β*-phenylpropionic acid.

4-Phenyl-2-amino-4-acetyl-*m*-tolylamine, and its acetyl derivative (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 18.

3-Phenyl-5-*p*-aminobenzylidenerhodanine (Andreasch), A., i, 663.

***ν*-Phenyl-*β*-*p*-aminobenzylidenethiocarbimideglycollide.** See 2:4-Diketo-3-phenyl-5-*p*-aminobenzylidenethiazolidine.

1-Phenyl-4-*α*-aminoethylidenepyrazol-5-one-3-carboxylic acid, ethyl ester (Benary, Reiter, and Soenderop), A., i, 253.

Phenyl*iso*amylparabanic acid (Stieger), A., i, 172.

Phenyl*iso*amylthioparabanic acid (Stieger), A., i, 172.

***β*-Phenyl-*α*-anisylacrylic acid** (Jörlander), A., i, 344.

5-Phenyl-3-anisyl-4:5-dihydro*iso*oxazole, hydroxy- and oximino- (Jörlander), A., i, 223.

***β*-Phenylanisylpropionic acids,** *α*-hydroxy- (Jörlander), A., i, 344.

5-Phenyl-3-anisylpyrazole, and its acetyl derivative (Jörlander), A., i, 223.

5-Phenyl-3-anisylpyrazoline, 4-hydroxy-, and its derivatives (Jörlander), A., i, 223.

Phenyl-2′-anthraquinonylsulphone, 2:5-*di*hydroxy- (Hinsberg), A., i, 575.

Phenylarsine-*p*-carboxylic acid (Sieburg), A., i, 486.

Phenylarsinic acid, *p*-amino-, thiocarbamide compounds of (Thoms), A., i, 359.

1-Phenylaziminobenzene, 5-cyano-. See 1-Phenylbenzo-1:2:3-triazole, 9-cyano-.

Phenylazocarbonamide, oxidation of (Angeli), A., i, 417.

Phenylazoformaldoximecarboxylic acid, methyl ester (Busch, Achterfeld, and Seuffert), A., i, 231.

Phenylazomeconin (Mitter and Sen), T., 991.

Phenylazonitromeconin (Mitter and Sen), T., 992.

4-Phenylbenzaziminol, 6-nitro- (Borsche and Scholten), A., i, 390.

1-Phenylbenz-1:2:3-triazole, 9-cyano- (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 17.

3-Phenyl-2-benzyl-1-benzylideneindene (Orechov and Grinberg), A., i, 451.

***o*-Phenylbenzyldi(*p*-dimethylamino)triphenylcarbinol,** and its hydrochloride (Pérard), A., i, 653.

***o*-Phenylbenzyldi(*p*-dimethylamino)triphenylmethane** (Pérard), A., i, 651.

***o*-Phenylbenzyl-*p*-diethylamino-*p*-dimethylaminotriphenylmethane,** and its hydrochloride (Pérard), A., i, 653.

Phenyl benzyl diketone, derivatives of (Jörlander), A., i, 344.

Phenyl-*β*-benzylhydrazine, *o*-amino-, and its derivatives (Franzen and v. Fürst), A., i, 58.

***ν*-Phenyl-*β*-benzylidene*iso*thiohydantoin.** See 4-Keto-3-phenyl-5-benzylidenethiazolidine, 2-imino-.

3-Phenyl-1:2-benzylidenetriazole, 5-thiol- (Bailey and McPherson), A., i, 588.

3-Phenyl-2-benzylindene (Orechov and Grinberg), A., i, 450.

d- and *l*-**Phenylbenzylmethylallylammonium hydroxide,** salts of, with bromocamphor-*π*-sulphonic acids (Reilly), T., 20; A., i, 129.

3-Phenyl-2-benzylquinoxaline, 3-*p*-chloro- (Jörlander), A., i, 345.

3-Phenyl-1-benzyl-1:2:4-triazole, 5-hydroxy- (Bailey and Moore), A., i, 356.

Phenyl *αβ*-*di*bromo-*β*-*m*-bromo-*p*-methoxyphenylethyl ketone (Kohler and Conant), A., i, 568.

Phenyl *m*-bromo-*p*-methoxystyryl ketone (Kohler and Conant), A., i, 568.

1-Phenyl-4-*p*-bromophenyl-3-methyldipyrazole (Michaelis and Rojahn), A., i, 480.

***β*-Phenyl-*α*-bromopropionic acid,** kinetics and dissociation constant of (Senter and Martin), T., 447; A., ii, 301.

α-Phenyl-$\Delta^{\alpha\gamma}$-butadiene, polymerisation of (Lebedev and Ivanov), A., i, 126.

Phenyl-*n*-butylhydrazine, and its hydrochloride (Reilly and Hickinbottom), T., 1028.

***γ*-Phenylbutyric acids,** *αα*-*di*bromo-, and *αα*-*di*iodo-, and their salts (Bougault), A., i, 26.

Phenylcarbamides, amino-, and their chloroacetyl derivatives (Jacobs and Heidelberger), A., i, 553, 583.

***α*-Phenylcarbamyl-*β*-benzylhydrazine** (Bailey and McPherson), A., i, 587.

3-Phenyl-5-*m*-carboxybenzylidenerhodanine (Andreasch), A., i, 663.

1-Phenyl-4-*o*- and -*p*-carboxyphenyl-3-methyldipyrazoles (Michaelis and Rojahn), A., i, 481.

Phenyl-*p*-chlorophenyl-*p*-bromophenylcarbinol, and its chloride (Stagner), A., i, 24.

Phenyl-*p*-chlorophenyl-*p*-bromophenylmethylamine, and its hydrochloride (Morgan), A., i, 21.

Phenyl-*p*-chlorophenyl-*p*-bromophenylmethylchloroamine (Morgan), A., i, 21.

Phenyl-*p*-chlorophenyl-*p*-bromophenylmethylhydroxylamine, and its hydrochloride (Stagner), A., i, 24.

1-Phenyl-4-*o*-chlorophenyl-3-methyldipyrazole (Michaelis and Rojahn), A., i, 480.

α-Phenylcinnamoylsemicarbazide, and its hydrochloride (Bougault), A., i, 689.

Phenyl cinnamylidenemethyl ketone, action of acetylacetone with (Scholtz), A., i, 462.

Phenyl-Δ^{α}-crotonic acid (Bougault), A., i, 335.

γ-Phenylcrotonic acids, α-bromo-, and α-iodo- (Bougault), A., i, 26.

Phenyl cyanostyryl ketone, and its derivatives (Kauffmann and Jeutter), A., i, 395.

α-Phenyl-ββ-di*iso*amylethylene glycol (Coma y Roca), A., i, 266.

Phenyldi-*p*-anisylacetaldehyde, and its derivatives (Coma y Roca), A., i, 266.

α-Phenyl-ββ-di-*p*-anisylethane (Coma y Roca), A., i, 266.

α-Phenyl-ββ-di-*p*-anisylethylene (Coma y Roca), A., i, 266.

α-Phenyl-αβ-di-*p*-anisylethylene glycol (Coma y Roca), A., i, 266.

Phenyldi-*p*-anisylmethane (Coma y Roca), A., i, 266.

β-Phenyl-αα-di-*p*-anisylpropaldehyde, and its oxime (Coma y Roca), A., i, 266.

γ-Phenyl-αβ-di-*p*-anisylpropylene glycol (Coma y Roca), A., i, 266.

4-Phenyl-2:6-dianisylpyranol (Dilthey), A., i, 579.

4-Phenyl-2:6-dianisylpyryl salts (Dilthey), A., i, 579.

β-Phenyl-αα-dibenzylethylene. See αγ-Diphenyl-β-benzylidenepropane.

Phenyldi-*p*-bromophenylmethylhydroxylamine, and its hydrochloride (Stagner), A., i, 24.

α-Phenyl-ββ-di*iso*butylethylene glycol (Coma y Roca), A., i, 266.

Phenyldi-*p*-chlorophenylmethylamine hydrochloride (Morgan), A., i, 21.

Phenyldi-*p*-chlorophenylmethylchloroamine (Morgan), A., i, 21.

Phenyldi-*p*-chlorophenylmethylhydroxylamine, and its hydrochloride (Stagner), A., i, 24.

10-Phenyl-9:9-di(-*p* diethylaminophenyl)-10-*p*-diethylaminophenyl-9:10-dihydroanthracene (Pérard), A., i, 652.

10-Phenyl-9:9-di(-*p*-diethylaminophenyl)-9:10-dihydroanthracene, 10-hydroxy- (Pérard), A., i, 652.

10-Phenyl-9:9-di(-*p*-dimethylaminophenyl)-10-*p*-diethylaminophenyl-9:10-dihydroanthracene (Pérard), A., i, 652.

10-Phenyl-9:9-di(-*p*-dimethylaminophenyl)-9:10-dihydroanthracene, and 10-hydroxy- (Pérard), A., i, 652.

Phenyldiglycine, *p*-amino-, acetyl derivative (Jacobs and Heidelberger), A., i, 584.

4-Phenyl-3:4-dihydro-1:2-benzopyrone, 5:7-*di*- and 4:5:7-*tri*-hydroxy-, and their derivatives (Fischer and Nouri), A., i, 469.

1-Phenyl-4:5-dihydro-1:2:4-triazole-5-one 3-methyl sulphone, tautomerism of, and its salts (Acree, Lubs, and Wilkins), A., i, 479.

10-Phenyl-10-*p*-dimethylaminophenyl-9:9-di(-*p*-diethylaminophenyl)-9:10-dihydroanthracene (Pérard), A., i, 652.

10-Phenyl-9-*p*-dimethylaminophenyl-9-diethylaminophenyl-9:10-dihydroanthracene, 10-hydroxy- (Pérard), A., i, 652.

10-Phenyl-9-*p*-dimethylaminophenyl-9:10-dihydroanthracene (Pérard), A., i, 651.

2-Phenyl-1:4-dimethyl*cyclo*pentadiene dihydropyridazine, 6-nitro- (Hale), A., i, 56.

1-Phenyl-2:3-dimethyl-5-pyrazolone. See Antipyrine.

3-Phenyl-5:8-dimethylquinoline, 4-hydroxy- (Wislicenus, Börner, Kurtz, and Bilhuber), A., i, 269.

2-Phenyl-3:3-dimethyltetrahydropyridine (Haller and Ramart-Lucas), A., i, 665.

1-Phenyl-4-diphenylmethylpyrazol-5-one (Wislicenus and Eble), A., i, 272.

1-Phenyl-4-diphenylmethylpyrazol-5-one-3-carboxylic acid, ethyl ester (Wislicenus and Eble), A., i, 272.

Phenyl diphenylmethyl sulphone (Hinsberg), A., i, 329.

p-**Phenylene-*n*-butyldiamine,** and its salts (Reilly and Hickinbottom), T., 1032.

o-**Phenylenediacetic acid,** and its ethyl ester (v. Braun, Kruber, and Danziger), A., i, 131.

p-**Phenylenediamine,** action of hydrogen peroxide with (Heiduschka and Goldstein), A., i, 482.

o-**Phenylenediamine,** 4-cyano- (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 17.

o-**Phenylenedicinnamoyldiamine,** *p*-nitro- (Kym and Jurkowski), A., i, 176.

o-**Phenylenedioxyacetic acid,** amino-, and nitro- (Jacobs and Heidelberger), A., i, 697.

Phenylethanol, *p*-hydroxy-. See Tyrosol.

Phenyl β-ethoxalylamino-Δ^{α}-propenyl ketone (Benary, Reiter, and Soenderop), A., i, 254.

α-Phenylethylacetoacetic acid, ethyl and menthyl esters (Rupe and Wild), A., i, 539.

Phenylethylcarbinol, amino-. See α-Phenylpropyl alcohol, β-amino-.

Phenylethylcyanoacetamide (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 475.

Phenylethylhydantoin, and *p*-chloro- (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 475.

Phenyl ethyl ketone, 6-bromo-2-hydroxy- (Simonis), A., i, 580.

α-Phenyl-β-ethylpentyl alcohol, and its acetate (Dumesnil), A., i, 654.

Phenyl-6-fluorones, *tri*hydroxy-9-*o*-*p*-*di*hydroxy- (Ghosh and Watson), T., 828.

Phenylglyceric acid, resolution of, into its active components (Rieber and Berner), A., i, 562.
  crystallography of (Goldschmidt), A., i, 561.

β-Phenylglutaconmethylimide, and its salts (Knust and Mumm), A., i, 415.

Phenylglycine, *p*-hydroxy- (Meldola, Foster, and Brightman), T., 551; A., i, 454.

Phenylglycines, amino-, and their derivatives (Jacobs and Heidelberger), A., i, 583.

Phenylhydrazides of acids of the sugar group, and their constitution and rotatory power (Hudson), A., i, 318; (Levene and Meyer), A., i, 631.

α-Phenylhydrazido-2-nitro-4-carbomethoxybenzyl methyl ketone (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 16.

Phenylhydrazine, action of, on opianic acid, nitro-opianic acid, and phthalonic acid (Mitter and Sen), T., 988; A., i, 710.

Phenylhydrazine, *p*-amino-, acetyl derivative, and its derivatives (Franzen and v. Fürst), A., i, 59.
  m-nitro-, preparation of (van der Haar), A., i, 228.

β-*N*-Phenylhydrazinoethyl anisyl ketone, α-hydroxy-, derivatives of (Jörlander), A., i, 223.

3-Phenyl-5-*mp*-*di*hydroxybenzylidenerhodanine (Andreasch), A., i, 663.

β-Phenyl-β-2-hydroxy-4:6-dimethoxyphenylpropion-amide and **ω-phenylhydrazide** (Fischer and Nouri), A., i, 470.

Phenylhydroxylamine, nitroso- (Baudisch), A., i, 356.
  nitroso-*m*-hydroxy-, ammonium salt (Baudisch and Klaus), A., i, 331.
  nitroso-*p*-hydroxy-, and its ammonium salt (Baudisch and Karzeff), A., i, 331.

Phenyl ω-hydroxystyryl ketone, and its benzoate, and *p*-chloro- (Jörlander), A., i, 341.

2-Phenylindazole, 3-hydroxy-, and its benzoate (Heller), A., i, 219.

1-Phenyl*iso*indazole, 4-bromo-, and 4-chloro- (Reich and Turkus), A., i, 585.
  5:7-*di*nitro- (Reich), A., i, 586.

Phenylindole, 3-bromo-2-*o*-amino- (Ruggli), A., i, 587.

3-Phenyl-5-ψ-indoxylidenerhodanine (Andreasch), A., i, 664.

Phenylketencarboxylic acid, methyl ester (Staudinger and Hirzel), A., i, 178, 630.

Phenylmalonanilic acid, methyl ester (Staudinger and Hirzel), A., i, 631.

Phenylmalonic acid, 2-nitro-4-cyano-, and 2:4-*di*nitro-, methyl esters (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 16.

Phenylmalon-*p*-toluidic acid, methyl ester (Staudinger and Hirzel), A., i, 631.

Phenyl methoxystyryl ketones, and their derivatives (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 208.

Phenylmethylacridinium salts, chromoisomerism of (Kehrmann and Stahrfoss), A., i, 221.

1-Phenyl-2-methylbenziminazole, 5-cyano- (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 16.

α-Phenyl-β-methylbutyl alcohol, and its acetate (Dumesnil), A., i, 654.

1-Phenyl 4-methyl-3-ethylpyrazole-5-one (Schroeter, Kesseler, Liesche, and Müller), A., i, 147.
2-Phenyl-3-methyl-3-ethyltetrahydropyridine, and its hydrochloride (Haller and Ramart-Lucas), A., i, 665.
Phenylmethylhydantoin (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 475.
Phenyl methyl ketoxime, rearrangement of, and its benzenesulphonate (Kuhara and Watanabe), A., i, 87.
Phenylmethylnitroamine, *tri*nitro-, preparation of (van Duin and van Lennep), A., i, 554.
α-Phenyl-ζ-methyloctan αγ-dione (*benzoylamylacetone*) (Rupe and Wild), A., i, 539.
α-Phenyl-β-methylpentyl alcohol, and its acetate (Dumesnil), A., i, 654.
α-Phenyl-4-methylstyrene, β-chloro- (v. Auwers), A., i, 34.
4-Phenyl-1-methyluracil, and its hydrochloride (Knust and Mumm), A., i, 415.
1-Phenylnaphthalene-*o*:3-dicarboxylic acid (Schaarschmidt and Georgeacopol), A., i, 275.
Phenyl-α-naphthylamine, preparation of (Katayama), A., i, 645.
Phenyl-β-naphthyldisulphone (Hinsberg), A., i, 135.
Phenyl-1′- and -2′-naphthylsulphones, 2:5-*di*hydroxy- (Hinsberg), A., i, 576.
Phenyl-Nile-blue, sulphonic acid from (Kehrmann and Herzbaum), A., i, 593.
Phenyl-6-nitro-4-acetyl-*m*-tolylamine (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 18.
Phenyl-*m*-nitrobenzylglycollic acid (Bodforss), A., i, 225.
as- and *s*-**Phenyl-2:6-*di*nitrobenzylhydrazines** (Reich, Gaigailian, and Chaskelis), A., i, 595.
Phenyl-2:6-*di*nitrobenzylnitrosoamine (Reich, Gaigailian, and Chaskelis), A., i, 595.
2-Phenyl-2-*m*-nitrobenzylquinoxaline (Bodforss), A., i, 225.
Phenyl *m*-nitro-α-hydroxystyryl ketones, and their derivatives (Bodforss), A., i, 224.
3-Phenyl-5-*m*-nitrophenylpyrazole, and its acetyl derivative (Bodforss), A., i, 225.
Phenylnorcodeine, *op*-*di*amino-, *p*-nitro-, and *op*-*di*nitro-, and their derivatives (v. Braun and Kindler), A., i, 164.
Phenylopiazone (Mitter and Sen), T., 992.
δ-Phenylpentan-β-one (Rupe and Wild), A., i, 539.
2-Phenylpentoxazoline, 5-hydroxy- (Gabriel and Ohle), A., i, 563.
Phenylphenosafraninesulphonic acid (Kehrmann and Herzbaum), A., i, 592.
1-Phenyl-3-ω-phenylethyl*cyclo*hexane (Lebedev and Ivanov), A., i, 127.
1-Phenyl-2:5-*endo*phenylvinylene-Δ^{1}-*cyclo*hexen-3-one (Scholtz), A., i, 462.
Phenylphthalazonecarboxylic acid (Mitter and Sen), T., 993.
Phenylpropiolic acid, *p*-nitrobenzyl ester (Reid), A., i, 334.
Phenylpropioltoluidides, thio-, and their sodium salts (Worrall), A., i, 336.
β-Phenylpropionic acid, *p*-nitrobenzyl ester (Lyman and Reid), A., i, 334.
β-Phenylpropionic acid, α-amino-, *p*-nitrobenzyl ester (Lyons and Reid), A., i, 559.
  p-hydroxy-. See Phloretic acid.
α-Phenylpropionitrile, α-*p*-nitro- (Opolski, Kowalski, and Pilewski), A., i, 25.
Phenylpropionylhydroxylamide (Bougault), A., i, 695.
α-Phenylpropyl alcohol, β-amino-, and its derivatives (Eberhard), A., i, 392.
Phenyl*iso*propylamine nitrite (Brander), A., i, 555.
α-Phenyl*iso*propylcarbamic acid, ethyl ester (Brander), A., i, 560.
Phenyl*iso*propylcarbamide (Brander), A., i, 556.
Phenylpyruvic acid, derivatives of (Hemmerlé), A., i, 394.
Phenylpyruvic acids, bromocyano-, salts and derivatives of (Opolski, Czaporowski, and Zacharski), A., i, 29.
2-Phenylquinoline-4-carboxylic acid, preparation of amino-derivatives of (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 54.
  amide and tetra-acetyldextrose derivative of (Karrer), A., i, 540.
  compounds of salicylic acid and (Lilly & Co.), A., i, 96.
Phenylresorcinol*tetra*chlorophthalein, and its diacetate (Orndorff and Murray), A., i, 339.
3-Phenylrhodanine-5-acetamide (Kallenberg), A., i, 280.
Phenyl*iso*rosindulinesulphonic acid (Kehrmann and Herzbaum), A., i, 593.
Phenyl*apo*safranine (Kehrmann and Speitel), A., i, 415.

Phenylsemicarbazide (Bailey and McPherson), A., i, 588.

1-Phenyl-5-styryl-Δ¹-*cyclo*hexen-3-one, and its derivatives (Scholtz), A., i, 462.

Phenyl styryl ketone, additive compound of perchloric acid and (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 209.

Phenylsuccinic acid series (Wren and Still), T., 513, 1019; A., i, 456.

Phenyltartramic acid (*tartranilic acid*), and its salts and derivatives (Casale), A., i, 546.

Phenyl *pp′*-tetramethyl*di*aminodiphenylmethyl sulphone (Hinsberg), A., i, 328.

Phenyl-*p*-tolylcarbamide (Mayer), A., i, 144.

Phenyltolyl*tetra*chlorophthalide, and hydroxy- (Orndorff, Murray, and Allen), A., i, 338.

1-Phenyl-4-*p*-tolyl-3:6-dimethyldipyrazole (Michaelis and Rojahn), A., i, 481.

Phenyl-*p*-tolylethane, and *di*chloro- (v. Auwers), A., i, 34.

1-Phenyl-4-*o*- and -*p*-tolyl-3-methyl-dipyrazoles (Michaelis and Rojahn), A., i, 480.

10-Phenyl-9:9:10-tri(-*p*-dimethylaminophenyl)-9:10-dihydroanthracene (Pérard), A., i, 652.

β-Phenyl-β-2:4:6-trimethoxyphenylpropionic acid (Fischer and Nouri), A., i, 470.

Phloretic acid, and its derivatives (Fischer and Nouri), A., i, 393.

Phloretin, synthesis of (Fischer and Nouri), A., i, 393.

Phloroglucinol, condensation of unsaturated nitriles with (Fischer and Nouri), A., i, 469.
detection of, and its distribution in plants (Joachimowitz), A., i, 682.
estimation of, by means of furfuraldehyde (Votoček), A., ii, 156.

Phospham (Dafert and Uhl), A., ii, 293.

Phosphate rock, estimation of phosphoric acid in (Semple), A., ii, 505.

Phosphorites, deposits of (Samoilov), A., ii, 489; (Schaller), A., ii, 490.

Phosphor-tin, analysis of, volumetrically (Lee, Fegely, and Reichel), A., ii, 427.

Phosphorus, allotropy of (Smits and Bokhorst), A., ii, 30; (Terwen), A., ii, 173.
dissociation of (Trautz), A., ii, 74.
poisoning. See under Poisoning.

Phosphorus:—
Phosphoric acid, extraction of, from soils (Hale and Hartley), A., ii, 41.
estimation of (Shuey), A., ii, 269.
estimation of, and phosphates, by alkalimetry (Smith), A., ii, 330.
estimation of, in phosphate rock (Semple), A., ii, 505.
estimation of, volumetrically, with uranium acetate (Thomlinson), A., ii, 41.
estimation of, in soils (Smith), A., ii, 100.
Orthophosphoric acid, molecular weight of (Balareff), A., ii, 85.
acidimetric estimation of (Balareff), A., ii, 101.
Phosphates in human blood-serum (Feigl), A., i, 520.
removal of, in qualitative analysis (Gattermann and Schindhelm), A., ii, 41.
Hypophosphoric acid, basicity of (Müller), A., ii, 30.
Metaphosphoric acid, velocity of hydration of (Balareff), A., ii, 23.
Pyrophosphoric acid, structure of (Balareff), A., ii, 467.
molecular weight of (Balareff), A., ii, 85.
estimation of, volumetrically (Balareff), A., ii, 506.
Perphosphates, preparation of (Aschkenasi), A., ii, 467.
Superphosphates, use of, as manures (Barbieri), A., i, 312.

Phosphorus organic compounds:—
Phosphoric acid, dialkyl esters of, preparation and ionisation of (Drushel and Felty), A., i, 126.

Phosphorus estimation:—
estimation of, in cast iron (Cavazzi), A., ii, 540.
estimation of, in iron and steel (Friedrich), A., ii, 536.
estimation of, in zinc phosphide (Liberi), A., ii, 329.
estimation of, in soils (Rost), A., ii, 579.

Phosphoryl chloride, action of, on ethyl and methyl alcohols (Balareff), A., i, 625.

Phosphotungstic acid, precipitated, fractionation of (Funk), A., i, 52.

Photogenin (Harvey), A., i, 365.

Photometer, ultra-violet (Lankshear), A., ii, 283.

Photophelein (Harvey), A., i, 365.

Phrenosin, and its derivatives (Levene and West), A., i, 657.

Phthaleins (ORNDORFF and MURRAY), A., i, 339.
  absorption spectra of (MOIR), A., ii, 349, 557.
Phthalic acid, metallic salts of (EKELEY and BANTA), A., i, 338.
  mixed esters of (REID), A., i, 456.
Phthalic acid, *di*- and *tetra*-chloro-, and 3-nitro-, *p*-nitrobenzyl esters (LYONS and REID), A., i, 559.
*iso***Phthalic acid**, 5-amino-, and its derivatives, and 5-nitro-, reduction of (MEYER and WESCHE), A., i, 341.
Phthalic acids, *p*-nitrobenzyl esters (LYMAN and REID), A., i, 334.
Phthalic anhydride, action of, on 1:6-dihydroxynaphthalene (FISCHER and KÖNIG), A., i, 661.
Phthalimidobenzenesulphonemethylethylenediamine (JOHNSON and BAILEY), A., i, 9.
Phthalimidobenzylsulphone-ethylenediamine (JOHNSON and BAILEY), A., i, 9.
Phthalimidophenylsulphone-ethylenediamine (JOHNSON and BAILEY), A., i, 10.
Phthalonic acid, preparation and derivatives of (TCHERNIAC), A., i, 33.
  action of phenylhydrazine on (MITTER and SEN), T., 988; A., i, 710.
Phthalyl chloride, reaction of, with benzene (COPISAROW), T., 10; A., i, 144.
5-*iso*Phthalylidene-bis-3-phenylrhodanine (ANDREASCH), A., i, 663.
5-*iso*Phthalylidene-bis-rhodanine (ANDREASCH), A., i, 663.
Phthalylidenedimalonylthiocarbamide, 3:4-*di*hydroxy- (DOX and PLAISANCE), A., i, 53.
Physiological action and chemical constitution, relation between (PYMAN), T., 167, 1103; A., i, 304.
Physiological fluids, substitution of potassium by radium in (ZWAADEMAKER and FEENSTRA), A., i, 241.
  estimation of chlorides in (HARDING and MASON), A., ii, 501.
Phytic acid and its salts, from wheat (BOUTWELL), A., i, 374.
Phytosterol, separation of, from fats and oils (PRESCHER), A., ii, 514.
  separation and estimation of, by digitonin (PRESCHER), A., ii, 275.
α-Picoline, compounds of, with copper, lead and silver haloids (DATTA and SEN), A., i, 323.
Picolinic acid, metallic salts of (LEY and FICKEN), A., i, 707.
β-Picolinium palladi- and pallado-chlorides (GUTBIER, FELLNER, KRÄUTER, FALCO, KRELL, SCHULZ, and WOERNLE), A., i, 541.
Picric acid, colours of solutions of (DEHN and BALL), A., i, 556.
  detection of, and its derivatives (PECKER), A., ii, 158.
  detection of, in blood (TIXIER), A., ii, 584.
  detection of, in urine (YDRAC), A., ii, 51.
  estimation of, in presence of nitric and sulphuric acids (RICHARDSON), A., ii, 158.
Picryl azide (SCHRADER), A., i, 595.
Pidan (BLUNT and WANG), A., i, 102.
Piezo-chemical studies (COHEN and VALETON), A., ii, 566.
Pigments, nitrogenous, of molasses (FRIEDRICH), A., i, 544; (STANĚK), A., i, 545.
  from sugar refinery products (STANĚK), A., i, 544.
Pimelic acid, αβγε-*tetra*hydroxy-, and its disilver salt (BORSCHE), A., i, 118.
α-Pinene, isomerisation and derivatives of (PRINS), A., i, 90.
Pine oil, optical activity of (TSAKALOTOS), A., i, 577.
Pinguicula vulgaris, proteolytic enzymes of (DERNBY), A., i, 438.
Pinonaldehyde and its derivatives (HARRIES and V. SPLAWA-NEYMAN), A., i, 213.
Piperazine cacodylate (ASTRUC), A., i, 9.
Piperic acid, *p*-nitrobenzyl ester (LYONS and REID), A., i, 559.
Piperidine, action of, on sulphur organic compounds (RAFFO and BALDUZZI), A., i, 382.
Piperidinium palladochloride (GUTBIER, FELLNER, KRÄUTER, FALCO, KRELL, SCHULZ, and WOERNLE), A., i, 541.
4-Piperidinoacetophenone, 3-nitro-, and its derivatives (BORSCHE, STACKMANN, and MAKAROFF-SEMLJANSKI), A., i, 18.
4-Piperidinobenzoic acids, amino- and nitro-, and their nitriles (BORSCHE, STACKMANN, and MAKAROFF-SEMLJANSKI), A., i, 17.
3-Piperidino-*p*-tolyl methyl ketone, 6-nitro- (BORSCHE, STACKMANN, and MAKAROFF-SEMLJANSKI), A., i, 18.
Piperidone, 3-amino-5-hydroxy-, 3-benzoyl derivative (HAMMARSTEN), A., i, 82.
o-**Piperidylmethylbenzyl alcohol**, and its salts (V. BRAUN), A., i, 170.
"**Piperidyltetrahydro*iso*quinolinium hydroxide**," and its salts (V. BRAUN), A., i, 169.

- **Piperonal,** 6-chloro- (Orr, Robinson, and Williams), T., 946 ; A., i, 703.
- **Piperonaldimethylacetal,** nitro- (Robinson), T., 120.
- **Piperonylic acid,** 6-chloro- (Orr, Robinson, and Williams), T., 948.
- **Piperonylideneacetone.** See 3:4-Methylenedioxystyryl methyl ketone.
- **Piperonylmethylhydantoin** (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 475.
- **Pipette,** automatic suction attachment for (Schroeder), A., ii, 418.
- **Pisanite** from Carinthia (Leitmeier), A., ii, 537.
- **Pituitary gland,** active principle of (Guggenheim ; Adams), A., i, 526.
- **Planerite,** gel form of (Leitmeier), A., ii, 494.
- **Plants,** biochemistry of (Stutzer), A., i, 439.
  - microchemistry of (Molisch), A., i, 505, 506, 507 ; ii, 387 ; (Tunmann), A., ii, 58.
  - green, constituents of (Curtius and Franzen), A., i, 438.
  - effect of accessory substances on growth of (Rosenheim), A., i, 503.
  - formation of unsaturated acids in (Komatsu), A., i, 139.
  - effect of ammonium salts on the physiology of (Söderbaum), A., i, 192.
  - benzene derivatives as nourishment for (Bokorny), A., i, 682.
  - physiological action of calcium in (Robert), A., i, 436.
  - catalase and oxydase in (Reed), A., i, 424.
  - distribution of catechol and phloroglucinol in (Joachimowitz), A., i, 682.
  - action of coal gas on (Wehmer), A., i, 507, 531, 618 ; (Doubt), A., i, 619.
  - of a copper-tailing district, occurrence of copper in (Bateman and Wells), A., i, 373.
  - deamidisation in (Schweitzer), A., i, 504.
  - formation of humus by (Troussov), A., i, 189.
  - containing hydroxymethylanthraquinones (Tunmann), A., i, 531.
  - manganese content of (Ehrenberg and Nolte), A., i, 504.
  - occurrence and estimation of methyl alcohol in (v. Fellenberg), A., i, 616.
  - nitrogenous metabolism in (Prianichnikov), A., i, 616.
  - diseased, nitrites and ammonia in (Boncquet), A., i, 74 ; (P. A. and M. Boncquet), A., i, 683.
- **Plants,** influence of organic compounds on the development of (Ciamician and Ravenna), A., i, 241, 681.
  - green, nutrition of, with organic compounds (Bokorny), A., i, 718.
  - action of oxydases in (Kastle and Buckner), A., i, 372.
  - oxydase activity in the tissues and juices of (Bunzell), A., i, 107.
  - preparation of pectic substances of (Schryver and Haynes), A., i, 245.
  - action of poisons on (Free), A., i, 683.
  - effect of potassium on the growth of (Weevers), A., i, 372 ; (Stoklasa), A., i, 682.
  - proteins in, food values of (Boruttau), A., i, 605.
  - in water cultures, action of radium on (Pilz), A., i, 718.
  - sand-culture experiments on nutrition of (McCall), A., i, 75.
  - value of sodium salts in nutrition of (Blanck), A., i, 624.
  - formation of starch in, exposed to light of various sources (Ursprung), A., i, 504.
  - detection of carotinoids in (van Wisselingh), A., ii, 554.
  - detection of flavones in, and their physiological significance (Shibata, Nagai, and Kishida), A., i, 107.
  - detection of iron in, microchemically (Wiener), A., ii, 44.
- **Plant cells,** permeability of (Stiles and Jörgensen ; Osterhout), A., i, 435.
  - specific action of barium salts on (Osterhout), A., i, 373.
- **Plant toxins,** inhibitive effect of soils on (Truog and Sykora), A., i, 622.
- **Plaster of Paris** (Keane), A., ii, 89.
- **Plasticity** (Podszus), A., ii, 245.
- **Platinum,** high-frequency spectrum of (Ledoux-Lebard and Dauvillier), A., ii, 283.
  - effect of poisonous gases on the photoelectric sensitiveness of (Krüger and Taege), A., ii, 119.
  - ionic mobility of (Lorenz and Posen), A., ii, 14, 15.
  - colloidal (Gutbier and Wagner), A., ii, 169.
  - action of burning coal gas on (Mylius and Hüttner), A., ii, 482.
  - **Platinous** nitrite, compounds of ammonia with (Tschugaev and Kiltinovic), A., ii, 96.
  - **Chloroplatinic acid,** preparation of (Rudnick and Cooke), A., ii, 264.
  - **Platinum organic compounds,** with unsaturated acids (Biilmann and Hoff), A., i, 123.

Platinum, estimation of, by precipitation (Ivanov), A., ii, 154.
  estimation of, microchemically, in presence of gold and silver (van Breukeleveen), A., ii, 155.
Podophyllin, extraction and estimation of (Tanzen), A., ii, 400.
Poison, cobra, action of, on lecithin (Kudicke and Sachs), A., i, 70.
Poisons, effect of, on enzymes (H. v. and B. Euler), A., i, 72.
  action of, on plants (Free), A., i, 683.
  purine metabolism after administration of (Pohl), A., i, 498.
Poisoning by phosphorus, metabolism in (Isaac; Isaac and Loeb), A., i, 678.
*iso***Poly-acids** (Rosenheim, Pieck, and Pinsker), A., ii, 35; (Rosenheim and Pieck), A., ii, 212.
Polymerisation (Briggs), T., 264; A., ii, 255.
Polymorphism and isomerism (Pfeiffer, Klinkert, and v. Pollitzer), A., i, 140.
Polypeptides, synthesis of (Abderhalden and Wybert), A., i, 119.
  isomerism of (Fischer), A., i, 381.
  decomposition of, by bacteria (Otsuka), A., i, 369.
  degradation of, by enzymes (Abderhalden and Fodor), A., i, 306.
  estimation of, in blood (Amann), A., ii, 54.
r-**Polypeptides,** hydrolysis of, by bacteria (Mito), A., i, 679.
Polyplumbates. See under Lead.
Polysilicates. See under Silicon.
Pomegranate tree, alkaloids of (Hess), A., i, 349; (Hess and Eichel), A., i, 350.
Poppy, anthocyanin of (Willstätter and Weil), A., i, 49.
Porphyrins, sensitising action of (Hausmann), A., i, 69.
  identification of, by spectroscopy (Schumm), A., i, 712, 715.
Potash deposits, chemical changes in (Rózsa), A., ii, 97; (Jänecke), A., ii, 265.
Potassium, influence of gases on the photoelectricity of (Wiedmann), A., ii, 6.
  effect of, on the growth of plants (Weevers), A., i, 372; (Stoklasa), A., i, 682.
  substitution of, by radium in physiological fluids (Zwaardemaker and Feenstra), A., i, 241.
Potassium alloys with mercury, electrical conductivity of (Hine), A., ii, 287.
Potassium salts, recovery of, from mineral silicates (Frazer, Holland, and Miller), A., ii, 570.
Potassium dihydrogen arsenates and phosphates, crystal structure of (W. and D. Asch), A., ii, 449.
  hydrogen carbonate, use of, as an analytical standard (Bruhns), A., ii, 419.
  sodium carbonate (Bain and Oliver), A., ii, 87.
  chlorate, spontaneous infection of a solution of (Waterman), A., i, 502.
  chloride electrode. See Electrode.
    action of magnesium on solutions of (Getman), A., ii, 90, 258.
    and sulphate, ionisation of mixtures of sodium chloride and sulphur with (Smith and Ball), A., ii, 247.
  *di*chromate, conductivity measurements of the action of ferrous sulphate and (Edgar), A., ii, 288.
    use of, as a standard (Bruhns), A., ii, 266.
  iodide and iodine, compound of ethyl oxalate with (Skrabal), A., i, 378.
  *per*manganate, action of, on metals (Foster), A., ii, 175.
    titration of ferrous salts with (Neidle and Crombie), A., ii, 93.
  nitrate, electro-reduction of (Kliatchko and Binggely), A., ii, 355.
  nickel selenate (Tutton), A., ii, 415.
  silicates, equilibrium of (Morey and Fenner), A., ii, 370.
  stannichloride, preparation of (Druce), T., 418; A., ii, 309.
  sulphate, ionisation of (Müller), A., ii, 117.
  *per*sulphate, use of, as a reagent in organic chemistry (Datta and Sen), A., i, 329.
  magnesium sulphate, solubility of (van Klooster), A., ii, 471.
  polysulphides (Thomas and Rule), T., 1063.
Potassium organic compounds:—
  cyanide, rate of hydrolysis of (v. Zawidzki and Mieczyński), A., ii, 81.
  methyl sulphate, rate of hydrolysis of (v. Zawidzki and Zaykowski), A., ii, 84.
Potassium estimation and separation:—
  estimation of (Baxter and Kobayashi), A., ii, 270; (Hibbard), A., ii, 384; (Haff and Schwartz; Blumenthal, Peter, Healy, and Gott), A., ii, 507.

Potassium estimation and separation:—
  estimation of, in presence of sodium (TURKUS), A., ii, 385.
  estimation of, in vegetable ashes (PELLET), A., ii, 542.
  estimation of, recovery of perchlorates from (VÜRTHEIM), A., ii, 568.
  separation of sodium and (SPAR CHEMICAL CO.), A., ii, 87.
Potatoes as a source of protein in diet (ROSE and COOPER), A., i, 524.
Potential, difference of, due to movement of electrolytes (KRUYT), A., ii, 403.
  difference of, due to adsorption of ions (BAUR and KRONMANN), A., ii, 231.
  variation of, with current density (ATEN), A., ii, 163, 190.
  discharge, of ions (GHOSH), A., ii, 352.
Precipitates, washing of (LATHROP), A., ii, 367; (WEGELIN), A., ii, 462.
Pressure, effect of, on solubility (SILL), A., ii, 75.
"**Probnal.**" See α-Propylhexoylurethane.
Proline, 4-hydroxy-, benzoyl derivative and its copper salt (HAMMARSTEN), A., i, 82.
Propaldehyde, derivatives of (HARRIES and OPPENHEIM), A., i, 210.
*cyclo***Propane** derivatives (KOHLER and CONANT), A., i, 566, 568.
Δα-Propenyl methyl ketone, β-amino-, derivatives of (BENARY, REITER, and SOENDEROP), A., i, 253.
3-*iso*Propenylphenoxyacetic acid (V. AUWERS), A., i, 268.
Propionhydroxamic acid, and its salts and derivatives (JONES and NEUFFER), A., i, 326.
Propionic acid, distillation of, in steam (RICHMOND), A., i, 316.
  ethyl ester, viscosity of the system stannic chloride and (KURNAKOV and BEKETOV), A., ii, 361.
  mercaptan esters of (FABER and REID), A., i, 626.
  methoxymethyl ester (CLARK, COX, and MACK), A., i, 316.
  p-nitrobenzyl ester (REID), A., i, 333.
Propionic acid, α-amino-, *p*-nitrobenzyl ester (LYONS and REID), A., i, 559.
  α-bromo-, phenyl ester (V. AUWERS and HILLIGER), A., i, 37.
   action of sodium methoxide with (MADSEN), A., ii, 250.
  β-bromo-, and β-chloro-, preparation of (JACOBS and HEIDELBERGER), A., i, 534.
Propionic acid, αβ-*di*bromo-, action of potassium iodide on (BILLMANN), A., i, 378.
  β-cyano- (DAKIN), A., i, 542.
  β-hydroxy-, azide and hydrazides of, and their derivatives (CURTIUS and AUFHÄUSER), A., i, 637.
n-**Propoxyacetic acid**, ethyl ester, hydrazide of, and its derivatives (CURTIUS and VAN DER LAAN), A., i, 636.
n-**Propoxyacetylazide** (CURTIUS and VAN DER LAAN), A., i, 636.
5-*n*-Propoxy-1:3-dimethyl-ψ-uric acid (BILTZ and STRUFE), A., i, 297.
β-**Propoxyethylidenemalonic acid**, ethyl ester (V. AUWERS and AUFFENBERG), A., i, 627.
n-**Propoxymethylurethane**, and its hydrochloride (CURTIUS and VAN DER LAAN), A., i, 636.
β-**Propoxypropylidenemalonic acid**, ethyl ester (V. AUWERS and AUFFENBERG), A., i, 627.
Propyl chloride, physical constants of (BERTHOUD), A., ii, 237.
*iso***Propyl alcohol**, α-amino-, picrate and hydrochloride of (GABRIEL and OHLE), A., i, 563.
  β-chloro-β′-amino-, and its salts and derivatives (GABRIEL and OHLE), A., i, 565.
Propylamine, physical constants of (BERTHOUD), A., ii, 237.
n- and *iso***Propylamine**, derivatives of (GABRIEL and OHLE), A., i, 563.
*iso***Propylammonium** palladi- and pallado-chlorides (GUTBIER, FELLNER, KRÄUTER, FALCO, KRELL, SCHULZ, and WOERNLE), A., i, 541.
p-*iso***Propylbenzylideneazobenzene-*p*-hydrazone** sulphate (TRÖGER and PIOTROWSKI), A., i, 668.
β-**Propylcinnamic acids**, stereoisomeric, and their derivatives (STOERMER, GRIMM, and LAAGE), A., i, 648.
αγ-**Propylene** oxide, preparation and properties of (DERICK and BISSELL), A., i, 1.
Propylenebis-(*o*-acetylaminophenyl) ether (JACOBS and HEIDELBERGER), A., i, 698.
α-**Propylhexoylurethane** (ODAIRA), A., i, 81.
*iso***Propylideneazobenzene-*p*-hydrazone**, and its sulphate (TRÖGER and PIOTROWSKI), A., i, 668.
Propyl mercaptan, γ-amino-, and its platinichloride (GRISCHKEVITSCH-TROCHIMOVSKI), A., i, 154.
Propylnorcodeine, γ-hydroxy-, and its derivatives (V. BRAUN and KINDLER), A., i, 164.

*iso***Propylpalladosammine** chloride (GUTBIER, FELLNER, KRÄUTER, FALCO, KRELL, SCHULZ, and WOERNLE), A., i, 542.

Propylphthalamic anhydride, βγ-*di*-hydroxy-, nitrosoamine of (GABRIEL and OHLE), A., i, 565.

n-**Propylphthalimide**, γ-bromo-, γ-chloro- and γ-iodo-β-hydroxy-, and βγ-*di*-hydroxy- (GABRIEL and OHLE), A., i, 563.

*iso***Propylphthalimide**, β-bromo-, β-chloro-, and β-hydroxy- (GABRIEL and OHLE), A., i, 564.

α-**Propylvalerylurethane** (ODAIRA), A., i, 81.

Proteins, chemistry of (HERZFELD and KLINGER), A., i, 300.
  optical activity of (RAKUZIN), A., ii, 286.
  specific action of (HEKMA), A., i, 420.
  adsorption of (RAKUZIN), A., ii, 124.
  resorption of (KJÖLLERFELDT), A., i, 605.
  action of bacteria on (ROBINSON and TARTAR), A., i, 498.
  action of bacteria on cleavage products of (SASAKI), A., i, 107.
  copper compounds of (OSBORNE and LEAVENWORTH), A., i, 98.
  action of nitric acid on (MÖRNER), A., i, 710, 711.
  compounds of silver salts and (PAULI and MATULA), A., i, 419.
  hydrolysis of, by water (GRAVES, MARSHALL, and ECKWEILER), A., i, 358.
  mechanical denaturation of (WIECHOWSKI), A., i, 520.
  inhibition of digestion of, by adsorbed tin salts (GOSS), A., i, 497.
  tryptic digestion of (LONG and HULL), A., i, 485.
  plant, food values of (BORUTTAU), A., i, 605.
  as supplements for corn gluten (OSBORNE, MENDEL, FERRY, and WAKEMAN), A., i, 237.
  of maize, oats, and wheat, effect of, on growth and development (MCCOLLUM, SIMMONDS, and PITZ), A., i, 185.
  in diet, relation of, to milk production (HART, HUMPHREY, and SURE), A., i, 608.
  of milk, influence of coagulation on the digestion of (LEARY and SHEIB), A., i, 184.
  animal, phosphorus in (LINDET), A., i, 60.
  removal of, from blood (GREENWALD), A., i, 523.

Proteins of the central nervous system (MCGREGOR), A., i, 185.
  detection of, in variegated leaves (LAKON), A., i, 504.
  estimation of arginine in (JANSEN), A., ii, 184.

Proteinuria, Bence-Jones (TAYLOR, MILLER, and SWEET), A., i, 368.

Proteolytic action, measurement of (SHERMAN and NEUN), A., ii, 111.

Protocatecualdehyde, preparation of (SCHMIDT), A., i, 272.

Protocatechuonitrile diacetate (HOESCH and V. ZARZECKI), A., i, 343.

Protopine (PERKIN), A., i, 280.

Protoplasm, effect of electrolytes on the permeability of (CLOWES), A., ii, 245.
  living, viscosity of (WEBER), A., i, 504.
  staining of, with colouring matters (SCHULEMANN), A., i, 369, 612; (SKRAUP), A., i, 612.

Prout's hypothesis (SCOTT), T., 288.

Prunicyanin, and its chloride (WILLSTÄTTER and ZOLLINGER), A., i, 45.

Prunus avium and *spinosa*, anthocyanins from (WILLSTÄTTER and ZOLLINGER), A., i, 45.

Prussian blue, hydrosol of (BACHMANN), A., i, 688.

Ptyalin, digestion of erythrodextrin by (BLAKE), A., i, 361.

Pump, mercury, for high pressures (KRAUS), A., ii, 567.

Purine metabolism. See Metabolism.

Purines, bioluminescence of (HELLER), A., i, 427.

Pyknometer, vacuum-jacketed (HALL), A., ii, 442.

Pyraconine, preparation and derivatives of (SCHULZE and LIEBNER), A., i, 470.

Pyraconitine, preparation and derivatives of (SCHULZE and LIEBNER), A., i, 470.

Pyramidone, periodides of (EMERY and PALKIN), A., i, 54.

Pyrargyrite from Hungary (LOCZKA), A., ii, 485.

Pyrazole, and its derivatives, absorption spectra of (ROZANOV), A., ii, 284.

Pyrazoles (MICHAELIS and ROJAHN), A., i, 480.

Pyrazoleanthrone-yellow, preparation of derivatives of (CHEMISCHE FABRIK GRIESHEIM ELEKTRON), A., i, 56.

Pyrethrum, manganese in (MCDONNELL and ROARK), A., i, 720.

Pyridine, thermo-chemistry of (MATHEWS, KRAUSE, and BOHNSON), A., ii, 238.

Pyridine, solubilities of substances in, and in its mixtures with water (Dehn), A., ii, 445.
  solubility of cupric chloride in (Mathews and Spero), A., i, 518.
  solubility of mercuric iodide in (Mathews and Ritter), A., ii, 300.
  complex compounds of acetylacetone, iron salts and (Weinland and Bässler), A., i, 6.
  compounds of phenol and cresols with (Hatcher and Skirrow), A., i, 665.
  compounds of the alkali metals with (Emmert), A., i, 221.
  compounds of, with bismuth, copper, lead and silver haloids (Datta and Sen), A., i, 323.
  action of, on sulphur organic compounds (Raffo and Balduzzi), A., i, 382.
Pyridine, 2-hydroxy-, curative properties of (Harden and Zilva), A., i, 612.
  2:4:6-*tri*hydroxy-, sodium salt and acetyl derivative of (v. Niementowski and Sucharda), A., i, 447.
Pyridines, hydroxy-, preparation and structure of (Williams), A., i, 353.
Pyridine-2-carboxylic acid, 4:6-*di*hydroxy- (*citrazinic acid*), ethyl ester (Wislicenus and Schöllkopf), A., i, 701.
Pyridone derivatives, inactivity of γ-carbonyl in (Schöttle), A., i, 166.
Pyrimidines (Johnson and Hadley), A., i, 585, 667.
Pyrites, dissociation pressure of (Allen and Lombard), A., ii, 194.
  estimation of sulphur in (Zay), A., ii, 328; (Phillips), A., ii, 379; (Craig), A., ii, 420.
Pyrogallol, oxidation of, with production of light (Goss; Harvey), A., ii, 436.
  potassium and sodium salts, relative value of, in absorption of oxygen (Anderson), A., ii, 39.
  di- and tri-methyl ethers, sulphonic acids, and *di*bromo- (Krauss and Crede), A., i, 558.
Pyrolusite, analysis of (Barnebey and Hawes), A., ii, 274; (Rupp; Barnebey and Bishop), A., ii, 390, 581.
Pyromucic acid, *p*-nitrobenzyl ester (Lyons and Reid), A., ii, 559.
Pyrone derivatives, inactivity of γ-carbonyl in (Schöttle), A., i, 166.
Pyroxenes, composition of (Doelter), A., ii, 378.
  rhombic and monoclinic (Ledoux), A., ii, 496.
Pyrrole, condensation products of (Tschelincev and Tronov), A., i, 411; (Tschelincev, Tronov, and Karmanov), A., i, 112.
  condensation of acetone with (Tschelincev and Tronov), A., i, 91, 93.
  and its derivatives, condensation of, with formaldehyde (Tschelincev and Maksorov), A., i, 164.
Pyrrole-2-aldehyde, condensation of ketones with (Lubrzynska), A., i, 52.
Pyrrole-black, nitroso- (Angeli and Cusmano), A., i, 413.
Pyrrolecarboxylic acids, saponification of esters of (Korschun and Gounder), A., i, 95.
Pyrroledicarboxylic acid, saponification of esters of (Korschun and Gounder), A., ii, 25.
Pyrrole-2:5-dicarboxylic acids, preparation of (Tschelincev and Maksorov), A., i, 165.
2-Pyrrolidyl propyl ketone, and its derivatives (Hess, Eichel, and Uibrig), A., i, 353.
"**Pyrrolidyltetrahydro*iso*quinolinium**" bromide (v. Braun), A., i, 169.
Pyruvic acid, production of, from lactic acid (Mazé and Ruot), A., i, 310.
  phenyl-2:6-*di*nitrobenzylhydrazone (Reich, Gaigailian, and Chaskelis), A., i, 595.
Pyrylium compounds (Dilthey), A., i, 578, 660.

Q.

Quartz sand, adsorption of ammonium sulphate by (Wolkoff), A., i, 622.
Quebrachine, identity of yohimbine and (Filippi), A., i, 582.
Quercetin, hydroxy-, synthesis of (Nierenstein), T., 4; A., i, 149.
Quinaketones (Kaufmann and Haensler), A., i, 472.
Quince seeds. See Seeds.
Quinidine, compound of mercuric nitrite and (Rây), T., 507; A., i, 470.
Quinine hydrogen sulphate, decomposition of (Howard and Chick), A., i, 581.
  compound of mercuric nitrite and (Rây), T., 507; A., i, 470.
Quinol, sulphonation of (Pinnow), A., ii, 528.
  behaviour of, in plants (Ciamician and Ravenna), A., i, 681.
  distinction between catechol, resorcinol and (Wolff), A., ii, 182.
Quinol*tetra*chlorophthalein (Orndorff and Kennedy), A., i, 347.

- **Quinoline,** compounds of, with bismuth, copper, lead and silver haloids (Datta and Sen), A., i, 323.
- **Quinoline,** 3-bromo-4-hydroxy- (v. Niementowski and Sucharda), A., i, 479.
- **Quinolines,** aminohydroxy-, and their derivatives (Jacobs and Heidelberger), A., i, 697.
- **Quinoline-3-carboxylamide,** 4-hydroxy- (v. Niementowski and Sucharda), A., i, 478.
- **Quinoline-3-carboxylamide-4-carboxylic acid,** 4-hydroxy- (v. Niementowski and Sucharda), A., i, 478.
- **Quinoline-2-carboxylic acid,** 3-bromo-4-hydroxy- (v. Niementowski and Sucharda), A., i, 479.
- **Quinoline-2:3-dicarboxylimide,** 4-hydroxy- (v. Niementowski and Sucharda), A., i, 478.
- *iso***Quinolinium** palladi- and pallado-chlorides (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.
- **Quinolone,** nitro-derivatives of (Kaufmann and de Petherd), A., i, 355.
- **4-Quinolylacetic acid,** and bromo-, ethyl esters and their salts (Rabe, Pasternack, and Kindler), A., i, 284.
- **4-Quinolyl bromomethyl ketone,** and its hydrobromide (Rabe, Pasternack, and Kindler), A., i, 284.
- **4-Quinolylketones** (Rabe, Pasternack, and Kindler), A., i, 283.
- **1-4′-Quinolylmethyl-5-ethylpiperidino-4-acetic acid,** ethyl ester, and its salts and derivatives (Rabe, Pasternack, and Kindler), A., i, 284.
- **Quinolyloxyacetic acids,** amino-, and their derivatives (Jacobs and Heidelberger), A., i, 697.
- **α-4-Quinolyl-β-piperidinoethyl alcohol,** and its salts (Rabe, Pasternack, and Kindler), A., i, 284.
- **4-Quinolyl piperidinomethyl ketone,** and its salts (Rabe, Pasternack, and Kindler), A., i, 284.
- **Quinone-imide colouring matters,** sulphonic acids from (Kehrmann and Herzbaum), A., i, 591.
- **Quinones,** action of acetaldehyde-ammonia on (Ghosh), T., 608 ; A., i, 517.

R.

- **Racemic acid,** *p*-nitrobenzyl ester (Lyman and Reid), A., i, 334.
- **Radiation** from black bodies, formula for calculation of (Schmidt), A., ii, 406.
- **Radioactive** compounds, luminous, decay of (Walsh), A., ii, 559.
  - elements, periodicity of (Hall), A., ii, 438.
    - nomenclature of (Fajans), A., ii, 523.
- **Radioactivity** of meteorites (Quirke and Finkelstein), A., ii, 576.
  - of water. See under Water.
- **Radio-elements.** See Radioactive elements.
- **Radium,** spectrum of (Anslow and Howell), A., ii, 401.
  - charged condition of the active deposits of (Henderson), A., ii, 351.
  - distribution of the active deposit of, in an electric field (Ratner), A., ii, 558.
  - concentration of, in carnotite ore (Loomis and Schlundt), A., ii, 31.
  - disintegration of (Choudhari), A., ii, 402.
  - action of penetrating rays from, on colloids (Fernau and Pauli), A., ii, 189.
  - as a substitute for potassium in physiological fluids (Zwaardemaker and Feenstra), A., i, 241.
  - emanation. See Niton.
  - action of, on plants (Pilz), A., i, 718.
  - standard solutions of (Moran), A., ii, 230.
- **Radium-*G*,** Röntgen ray spectra of lead and (Siegbahn and Stenström), A., ii, 524.
- *Radix althaeae.* See Marsh mallow.
- **Raffinose,** physiological behaviour of (Kuriyama and Mendel), A., i, 611.
  - estimation of, in molasses (Staněk), A., ii, 342.
- **Ragweed.** See *Ambrosia artemisifolia.*
- **Rain-water.** See under Water.
- *Ramalina cuspidata* and *scopulorum*, constituents of (Ryan and O'Riordan), A., i, 342.
- **Rays,** Röntgen, and crystallography (v. Laue), A., ii, 166.
  - action of, on crystals (Olie and Byl), A., ii, 286.
  - interference effects of crystals in (Debye and Scherrer), A., ii, 437.
  - absorption of (Aurén), A., ii, 350.
- **Reduction** without acid (Neidle and Crombie), A., ii, 93.
  - in presence of oxidising agents (Dhar), T., 690 ; A., ii, 458.
- **Refraction** of solutions (Blanc), A., ii, 229.
  - of colloidal solutions (Wiegner), A., ii, 185.

Refractive index, relation between density and (Rossický), A., ii, 453.
  of mineral carbonates (Gaubert), A., ii, 144.
  of unsaturated hydrocarbons (Englaar). A., i, 111.
Refractivity of oxygen and nitrogen compounds (Le Bas), A., ii, 549.
  of methylated nitroanilines and nitrosoamines (Jansen), A., ii, 101.
Rennin, detection of (Graber), A., ii, 60.
Resins, action of ozone on (Harries and Paulsen), A., i, 213.
Resorcinol, detection of, colorimetrically (Krauskopf and Ritter), A., ii, 48.
  distinction between catechol, quinol, and (Wolff), A., ii, 182.
β-Resorcinolglucoside and its pentacetyl derivative (Fischer and Bergmann), A., i, 468.
Respiration, effect of ethyl alcohol on, in man (Higgins), A., i, 489.
Rhamnose, sublimation of (Ghosh), A., i, 80.
Rhamnose-*p*-tolylhydrazone (van der Haar), A., i, 380.
Rheum, constituents of the rhizomes of (Tunmann), A., i, 531.
Rhizonic acid, synthesis of (Sonn), A., i, 143.
Rhodanines (Andreasch), A., i, 663.
  stereochemistry of (Kallenberg), A., i, 279.
Rhodeose, oximes and hydrazones of, and their derivatives (Votoček), A., i, 250.
Rhodium *tri*bromide and *tri*chloride (Gutbier and Hüttlinger), A., ii, 482.
  oxides (Gutbier, Hüttlinger, and Maisch), A., ii, 483.
Rhubarb, detection of (Beal and Okey), A., ii, 279.
Ricinus, seeds of. See Seeds.
Ring formation, studies in (Turner), T., 1; A., i, 130.
  with elimination of nitro-groups (Reich and Turkus; Reich), A., i, 585.
Rocks, equilibria in the formation and metamorphosis of (Niggli), A., ii, 457.
Roscherite (Slavík and Preis), A., ii, 145.
Rotation of optically active compounds, influence of constitution on (Rupe and Wild), A., i, 538; (Rupe and Silberstrom), A., ii, 435.
  of sugars (Foulkes; Mackenzie, and Ghosh), A., i, 79; (Hudson and Yanovsky), A., i, 445.
Rotatory power of liquid crystals (Gaubert), A., ii, 158.
Rubber. See Caoutchouc.
Rubidium chloride, melting point of, and freezing points of its mixtures with alkali chlorides (Richards and Meldrum), A., ii, 531.
  germano-, plumbi-, and stanni-fluorides (Skrabal and Gruber), A., ii, 261.
  nickel selenate (Tutton), A., ii, 415.
Rumex, detection of (Beal and Okey), A., ii, 279.
Ruthenium, action of oxygen on (Gutbier, Leuchs, Wiessmann, and Maisch), A., ii, 38.
  oxides (Gutbier, Leuchs, and Wiessmann), A., ii, 483.
Rutile, crystal structure of (Williams), A., ii, 450.

S.

Sabinols, isomeric, and their derivatives (Paolini and Rebora), A., i, 90.
"**Saccharin**" (*o-benzoicsulphinide*), detection and estimation of, in foods (Bonis), A., ii, 430.
ψ-Saccharinhydrazide. See 2-Hydrazino-1-benzsulphonazole.
Saccharophosphatase in yeast (Djenab and Neuberg), A., i, 680.
Salazinic acid, and its acetyl derivatives (Hesse), A., i, 458.
Salicylic acid, preparation of (Pomilio), A., i, 332.
  dissociation of (Christiansen), A., ii, 25.
  solubility of, in mixed non-aqueous solvents (Marden and Dover), A., ii, 243.
  ferric compounds of (Weinland and Zimmermann), A., i, 649.
  basic mercury salt, estimation of mercury in (Lajoux), A., ii, 273.
  tetra-acetyl-dextrose and -glucoside derivatives (Karrer), A., i, 540.
  p-aminophenyl ester, bromo-derivative of (Abelin and Lichtenstein-Rosenblat), A., i, 454.
  benzyl and methyl esters, compounds of thiocarbamide with (Taylor), T., 661; A., i, 514.
  methyl ester, analysis of (Albright), A., ii, 279.
  p-nitrobenzyl ester (Lyman and Reid), A., i, 334.
  phenyl ester (*salol*), estimation of, in presence of acetanilide and of phenacetin (Salkover), A., ii, 53.

- **Salicylic acid**, compounds of 2-phenylquinoline-4-carboxylic acid and (Lilly & Co.), A., i, 96.
  - occurrence of, and its salts in the animal organism (Scott, Thoburn, and Hanzlik), A., i, 241.
  - detection of, microchemically (Tunmann), A., ii, 552.
  - estimation of salts of (Elion), A., ii, 514.
  - estimation of, in foods (Steenbergen), A., ii, 549.
- **Salicylic acid**, amino- and nitro-derivatives of (Meldola, Foster, and Brightman), T., 536; A., i, 453.
  - 5-amino-, and 5-iodo-, *p*-nitrobenzyl esters (Lyons and Reid), A., i, 559.
  - 4-bromo- (Simonis), A., i, 580.
  - 3-nitro- (Simonsen and Rau), T., 232.
- **Salicylide**, *di*bromo- (Benary, Reiter, and Soenderop), A., i, 252.
- **Salicylideneazobenzene-*p*-hydrazone** salts (Tröger and Piotrowski), A., i, 668.
- **Salicylidene-*p*-chlorobenzeneazo-α-naphthylhydrazone** (Tröger and Piotrowski), A., i, 669.
- **Saligenin**, behaviour of, in plants (Ciamician and Ravenna), A., i, 681.
- **Salol.** See Salicylic acid, phenyl ester.
- **Salt deposits**, oceanic, equilibria in (D'Ans, Bertsch, and Gessner), A., ii, 176; (Jänecke), A., ii, 527.
- **Salts**, effect of light on the loss of water of crystallisation from (Beutel), A., ii, 63.
  - double, dissociation of aqueous solutions of (Maxwell), A., ii, 562.
  - internally complex (Ley and Ficken), A., i, 706.
  - molten, specific gravity and surface tension of (Jaeger and Kahn), A., ii, 69, 70.
  - effect of other salts on the solubility of (Harkins and Paine), A., ii, 75; (Harkins and Pearce), A., ii, 76, 77.
- *Salvia*, anthocyanin of (Willstätter and Bolton), A., i, 42.
- **Salvianin**, and its salts (Willstätter and Bolton), A., i, 42.
- **Salvin** and **Salvinin**, and their derivatives (Willstätter and Bolton), A., i, 42.
- **Samarium**, arc spectra of (Eder), A., ii, 185.
- **Sambunigrin**, synthesis of (Fischer and Bergmann), A., i, 657.
- **Santene**, synthesis of (Komppa and Hintikka), A., i, 214.
- **Saponins**, chemistry of (van der Haar), A., i, 41.
- **Saponins**, pharmacology of (van der Haar), A., i, 70.
- **Sarcosine**, β-naphthalenesulphonyl derivative (Bergell), A., i, 448.
- **Scapolite** from the Lacher See district (Brauns), A., ii, 325.
- **Scolopsite**, composition of (Thugutt), A., ii, 493.
- **Scopoline**, degradation of (Hess), A., i, 52, 162.
  - bromide, and its derivatives (Schmidt), A., i, 409.
- **Scurvy**, effect of diet on development of (McCollum and Pitz), A., i, 604.
- **Scyllitol**, preparation of, from *Scyllium canicula* (Rosenheim), A., i, 366.
- *Scyllium canicula* (dog-fish), preparation of scyllitol from (Rosenheim), A., i, 366.
- **Sea-urchin**, eggs of. See Eggs.
- **Sea-water.** See under Water.
- **Sebacic acid**, *p*-nitrobenzyl ester (Lyman and Reid), A., i, 334.
- α- and β-**Sedoheptitols**, and their benzylidene derivatives (La Forge and Hudson), A., i, 444.
- **Sedoheptose**, and its derivatives (La Forge and Hudson), A., i, 444.
- *Sedum spectabile*, sugar from the leaves and stem of (La Forge and Hudson), A., i, 144.
- **Seeds** of *Corchorus capsularis* (jute), raffinose in (Annett), A., i, 506.
  - of *Cydonia* (quince) as protective colloids (Gutbier and Wagner), A., ii, 131, 168, 169.
  - of *Hordeum vulgare*, absorption of solutions by (Brown and Tinker), A., i, 74.
  - of *Hydnocarpus alcalae* and of *Pangium edule*, constituents of (Brill), A., i, 719.
  - of *Ricinus*, hydrolysis of fats by lipase in (Tancov), A., i, 182.
- **Seladonite**, analyses of (Koenig), A., ii, 487.
- **Selenium**:—
  - **Selenic acid**, reduction of (Benger), A., ii, 568.
    - action of, on osmium (Hradecky), A., ii, 483.
- **Selenium**, estimation of, in bones, teeth and urine (Gassmann), A., ii, 540.
- **Selenophthaleins**, preparation of, and their halogen derivatives (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 204.
- **Seleno*iso*trehalose**, and its derivatives (Schneider and Wrede), A., i, 541.
- **Semicarbazide**, estimation of (Datta and Choudhury), A., ii, 108.

- **Semioxamazide**, estimation of (Datta and Choudhury), A., ii, 108.
- **Senna**, detection of (Beal and Okey), A., ii, 279.
- **Sericin**, derivatives of (Harries and Stanford), A., i, 213.
- **Serratulin** (Molisch), A., i, 507.
- **Serum**, optical activity of (Rakuzin), A., ii, 286.
  - action of salts on the complement of (Poyarkov), A., i, 427.
  - antidiphtheritic, adsorption of, by aluminium hydroxide (Rakuzin and Flier), A., i, 427.
  - antitoxic, concentration of (Homer), A., i, 497.
  - estimation of cholesterol, colorimetrically, in (Weston), A., ii, 156.
- **Sewage**, estimation of nitrates in (Phelps and Shoub), A., ii, 504.
- **Shaking apparatus** (Thoms), A., ii, 567.
- **Silicon**, thermoelectric properties of (Fischer and Baerwind), A., ii, 86.
- **Silicon compounds**, nomenclature of (Stock), A., ii 204.
- **Silicon** *tetra*fluoride, density of (Germann and Booth), A., ii, 173.
  - *di*oxide (*silica*), internal structure of (Kyropoulos), A., ii, 468.
    - equilibrium of anorthite, forsterite and (Boeke), A., ii, 147.
    - action of, with oxides of barium, calcium, and magnesium (Hedvall), A., ii, 205.
    - equilibrium of carbon dioxide and (Niggli), A., ii, 211.
    - biochemistry of (Gonnermann), A., i, 494.
    - estimation of (Hawley), A., ii, 332.
  - **Silicic acids**, formation of, from silicates (Tschermak), A., ii, 30.
  - **Silicates**, melting points of (Doelter), A., ii, 456.
    - fusion of (Neubauer), A., ii, 492.
    - exchange of bases in (Ramann and Spengel), A., ii, 468.
  - **Polysilicates** and polyplumbates (Kassner), A., ii, 314.
- **Silicon**, estimation of, in tungsten steel (van Duin), A., ii, 181.
- **Silver**, occurrence of, in galena ores (Nissen and Hoyt), A., ii, 144.
  - electrochemical equivalent of (Bovard and Hulett), A., ii, 354.
  - electro-hydrosols of (Rebière), A., ii, 571.
  - colloidal (Gutbier and Wagner), A., ii, 168; (Gutbier and Kräutle), A., ii, 298.
  - action of sulphides on (Hahn), A., ii, 371.
- **Silver alloys** with glucinum (Oesterheld), A., ii, 89.
  - with tellurium (Chikashige and Saito), A., ii, 139.
- **Silver salts**, electrical conductivity of, in pyridine (Mathews and Johnson), A., ii, 289.
  - ammoniates of (Bruni and Levi), A., ii, 470.
  - compounds of proteins with (Pauli and Matula), A., i, 419.
- **Silver** bromide, compounds of, with pyridine, α-picoline and quinoline bromides (Datta and Sen), A., i, 323.
  - chloride, reduction of (Gawalowski), A., ii, 88.
  - chromates, and their solid solutions with nitrates (Köhler), A., ii, 32.
  - haloids, double salts of alkali haloids and (Shemtschushni), A., ii, 140.
  - iodide, thermodynamic properties of lead iodide and (Taylor), A., ii, 14.
  - nitrate, electrical conductivity of (Sachanov), A., ii, 234.
  - peroxynitrate (Brown), A., ii, 88.
- **Silver estimation:—**
  - estimation of, gravimetrically (Murmann), A., ii, 38.
  - estimation of, in organic compounds (Lucas and Kemp), A., ii, 542.
- **Silver electrode.** See Electrode.
- **Silver ion**, determination of the transport number of (Krumreich), A., ii, 118.
- **Silver voltameter.** See Voltameter.
- **Skin**, pigment-forming enzyme of (Bloch), A., i, 675.
- **Sloe.** See *Prunus spinosa*.
- **Soap**, detergent action of (Pickering) T., 86; A., ii, 165.
  - physiological function of (Kende), A., i, 615.
  - estimation of free alkali in (Izmailski), A., ii, 153.
- **Soda-lime tube** (Kelley), A., ii, 43.
- **Sodamide**, syntheses by means of (Haller and Ramart-Lucas), A., i, 665.
- **Sodio-*p*-toluenesulphonchloroamide.** See Chloramine-T.
- **Sodium**, preparation of, as a lecture experiment (Wiechowski), A., ii, 568.
- **Sodium alloys** with lead in liquid ammonia (Smyth), A., ii, 473.
  - with mercury, electrical conductivity of (Hine), A., ii, 287.
  - with mercury and strontium, equilibrium of sodium and strontium chlorides with (Smith and Braley), A., ii, 455.
- **Sodium salts**, value of, in nutrition of plants (Blanck), A., i, 624.

Sodium arsenites (Schreinemakers and de Baat), A., ii, 206.
  borates, equilibrium of the formation of (Sborgi and Mecacci), A., ii, 138.
  *per*borate, preparation of (Deutsche Gold- & Silber-Scheideanstalt vorm. Roessler), A., ii, 139.
  *tetra*borate, water of crystallisation of (Hoffmann), A., ii, 206.
  carbonate, electrolysis of solutions of (van Laer), A., ii, 404.
    hydrolysis of (Seyler and Lloyd), T., 138; A., ii, 196.
  hydrogen carbonate, effect of bile on the reaction between oleic acid and (Kingsbury), A., i, 362.
  potassium carbonate (Bain and Oliver), A., ii, 87.
  *per*chlorate, use of, in micro-analysis (Denigès), A., ii., 345.
  chloride, pure (Shipper), A., ii, 571.
    growth and dissolution of crystals of, in solutions containing carbamide (Schnorr), A., ii, 469.
    equilibrium of solutions of strontium chloride and, with amalgams of sodium and strontium (Smith and Braley), A., ii, 455.
    and sulphate, ionisation in mixtures of potassium chloride and sulphate with (Smith and Ball), A., ii, 247.
  hydroxide, electrolytic preparation of (van Laer), A., ii, 404.
  hypochlorite, action of, on amides of hydroxy-acids (Weerman), A., i, 546.
Disodium nitrite (Maxted), T., 1016.
Sodium *per*oxide, use of, in thermochemistry (Mixter), A., ii, 123.
  phosphates (Smith), A., ii, 309.
  hydrogen phosphate, dehydration of (Balareff), A., ii, 88.
  polyphosphate, and its action on glass, platinum, and silica vessels (Smith), A., ii, 309.
  sulphate, absorption of light by aqueous solutions of (Hulbert and Hutchinson), A., ii, 557.
    transition points of (Jänecke), A., ii, 15.
  sulphates, equilibrium of (Pascal), A., ii, 248.
  sulphide, estimation of, in sulphide dye baths (Swann), A., ii, 385.
  polysulphides (Thomas and Rule), T., 1063.
  sulphite, photochemical oxidation of solutions of (Mathews and Weeks), A., ii 230.

Sodium organic compounds:—
  alkyls and aryls (Schlenk and Holtz), A., i, 256.
  benzyl cyanide, reaction of ethyl *p*-tolylcinnamate with (Daughters), A., i, 647.
  cyanide, hydrolysis of (Worley and Browne), T., 1057.
Sodium estimation and separation:—
  estimation of, in vegetable ashes (Pellet), A., ii, 542.
  estimation of, in presence of potassium (Turkus), A., ii, 385.
  separation of potassium and (Spar Chemical Co.), A., ii, 87.
Soils, artificial, preparation of (Gautier), A., i, 509.
  and their solutions (Nolte), A., i, 621.
  formation of layers in (Puchner), A., i, 532; (Ehrenberg, Hahn, and Nolte), A., ii, 453.
  action of salt solutions on the permeability of (Hissink), A., i, 509.
  adsorption by (Harris), A., ii, 443.
  absorption of organic dyes by (zu Leiningen), A., ii, 112.
  biological changes in (Allison), A., i, 243.
  action of frost on (Nolte and Hahn), A., i, 621.
  constituents of, which inhibit the action of plant toxins (Truog and Sykora), A., i, 622.
  ammonification in (Miyake), A., i, 718.
  ammonification and nitrification in (Lipman and Burgess), A., i, 243; (Miyake), A., i, 244; (Münter), A., i, 722.
  effect of paraffin on ammonification and nitrification in (Gainey), A., i, 721.
  fixation of ammonia in (McBeth), A., i, 511; (Koch), A., i, 622.
  absorption of ammonium salts by (Miyake), A., i, 247.
  effect of ammonium sulphate on (Allison and Cook), A., i, 621; (Wolkoff), A., i, 622.
  sterilisation of, with antiseptics (du Buisson), A., i, 529.
  effect of acids and alkalis on bacteria in (Gruzit), A., i, 430.
  influence of salts on bacteria in (Greaves), A., i, 243.
  colloids in (Wolkoff), A., i, 621.
  α-crotonic acid in (Walters and Wise), A., i, 376.
  isolation of cyanuric acid from (Wise and Walters), A., i, 622.
  ferrification in (Brown and Corson), A., i, 248.

Soils, effect of gypsum on (Nolte), A., i, 624.
  relation between the lime-requirement and the base-absorption capacity of (Schollenberger), A., i, 440.
  manurial experiments in (de Wilkoszewski), A., i, 723.
  nitrification in (Kelley), A., i, 431; (Gainey), A., i, 529; (Brown and Hitchcock), A., i, 717; (Gainey and Metzler), A., i, 722.
  distribution of organic nitrogen in (Morrow and Gortner), A., i, 512.
  soluble non-protein nitrogen of (Potter and Snyder), A., i, 75.
  organic matter of (Gortner), A., i, 248, 310, 311; (Gortner and Shaw), A., i, 376.
  formation of ortstein and laterite in (Stremme), A., i, 512.
  phosphorus in (Potter and Benton), A., i, 76.
  extraction of phosphoric acid from (Hale and Hartley), A., ii, 41.
  effect of bacteria on phosphates in (Hopkins), A., i, 431.
  effect of lime and magnesia on sulphur in (MacIntire, Willis, and Holding), A., i, 723.
  effect of sulphuric acid in, on the growth of beet (Andrlík), A., i, 620.
  distribution and estimation of water in (Alway and McDole), A., i, 509; (Bouyoucos), A., i, 510.
  calcareous, formation of "black alkali" in (Breazeale), A., i, 724.
  orthoclase-bearing, availability of potash in (Briggs and Breazeale), A., i, 511.
  peat, effect of sulphur in, on underground building work (Kühl; Thörner), A., i, 76.
    nucleic acid derivatives in (Bottomley), A., i, 724.
  effect of the reaction of, on the availability of ammonium sulphate (Cook and Allison), A., i, 623.
  determination of the reaction of (Christensen), A., i, 684.
  estimation of ammonia in (Baragiola and Schuppli), A., ii, 380.
  estimation of the total carbon in (Schollenberger), A., ii, 103.
  estimation of organic carbon in (Shorey and Fry), A., ii, 422.
  estimation of carbonates in (Hutin), A., ii, 541.
  estimation of nitrogen in (Latshaw), A., ii, 100.
  estimation of nitric nitrogen in (Greaves and Hirst), A., ii, 578.
Soils, estimation of nitrates in (Davis), A., ii, 329.
  estimation of phosphorus in (Rost), A., ii, 579.
  estimation of phosphoric acid in (Smith), A., ii, 100.
Soil solutions (van Zyl), A., i, 439.
  extraction and analysis of (Ramann, März, and Bauer), A., i, 311.
Solanine (Heiduschka and Sieger), A., i, 407.
Solids, constitution and properties of (Langmuir), A., ii, 19.
  black, radiation from (Schmidt), A., ii, 406.
  electric double-layer at the contact of liquids and (Frenkel), A., ii, 191.
  vapour pressure of (Schmidt), A., ii, 408.
Solubility, effect of pressure on (Sill), A., ii, 75.
  in mixed non-aqueous solvents (Marden and Dover), A., ii, 243.
  in water, pyridine, and in aqueous pyridine (Dehn), A., ii, 445.
  of acids, effect of neutral salts on (Henderson and Taylor), A., ii, 77.
  of non-electrolytes, influence of salts on (v. Euler and Svanberg), A., ii, 445.
  of salts, effect of other salts on (Harkins and Paine), A., ii, 75; (Harkins and Pearce), A., ii, 76, 77.
Solubility product, non-constancy of (Hill), A., ii, 242.
Solutions (Horiba), A., ii, 409, 410.
  theory of (Hartung), A., ii, 445.
  structure of (v. Weimarn), A., ii, 126.
  physical properties of, and their mixtures (Andersson), A., ii, 126.
  refraction of (Blanc), A., ii, 229.
  photoelectric ionisation of (Volmer), A., ii, 353.
  electrical conductivity of (Taylor and Acree), A., ii, 7, 8.
  aqueous-alcoholic, specific heat of (Kolosovski), A., ii, 65.
  osmotic theory of (Jellinek), A., ii, 294.
  evaporation of (Plaisance and Pervier), A., ii, 378.
  viscosity of (Arrhenius), A., ii, 443.
  influence of the solvent on equilibrium in (Smits), A., ii, 171.
  colloidal. See Colloidal solutions.
  non-aqueous (Curtis and Burns), A., ii, 260.

- **Solvents**, influence of electrolytes on the dissociation of (Sachanov), A., ii, 128.
  - application of Beer's law to (Stewart and Wright), T., 183; A., ii, 186.
- **Sorbite** (Dejean), A., ii, 535.
- *Sorghum vulgare*, occurrence and estimation of hydrocyanic acid in (Willaman), A., i, 245, 246.
- **Sozoiodol-mercury compounds** (Rupp and Herrmann), A., i, 516.
- **Sparteine**, solubility of (Valeur), A., i, 411.
  - detection of, microchemically (Tunmann), A., ii, 518.
- **Specific gravity.** See Density.
- **Specific volume.** See Volume.
- **Spectra** of the elements, and their classification (Kutter), A., ii, 185.
  - of organic colouring matters (Pokorný), A., ii, 402.
  - absorption (Lankshear), A., ii, 283.
    - and chemical constitution of organic compounds (British Association Reports), A., ii, 435.
    - of azo-compounds and their salts (Kehrmann and Hempel), A., i, 593.
    - of polyhydroxyanthraquinone colouring matters (Meek), T., 969; A., ii, 558.
    - of colouring matters (Ghosh and Watson), T., 815; A., ii, 523.
    - of indigo derivatives (Lifschitz and Lourié), A., i, 586.
    - of metal-ammines (Shibata and Matsuno), A., ii, 186.
    - of phthaleins (Moir), A., ii, 349, 557.
    - of pyrazole and its derivatives (Rozanov), A., ii, 284.
    - *of unsaturated substances* (Macbeth and Stewart), T., 829; A., ii, 522.
  - arc and spark, of metals (Takamine and Nitta), A., ii, 402.
  - emission (Stark), A., ii, 281.
  - high-frequency (Ledoux-Lebard and Dauvillier), A., ii, 283; (Siegbahn), A., ii, 402.
  - infra-red absorption, of diatomic gases (Brinsmade and Kemble), A., ii, 402.
  - Röntgen-ray, of crystals (Smits and Scheffer), A., ii, 78.
    - of isotopic elements (Siegbahn and Stenström), A., ii, 524.
  - ultra-violet absorption, quantitative light-filter for (Peskov), A., ii, 349.
    - of blood-sera (Lewis), A., ii, 62.
- **Spectrochemistry** of benzene derivatives (v. Auwers), A., i, 266.
- **Spinacene**, and its derivatives (Chapman), T., 56; A., i, 193.
- **Spleen**, enzymes of the (Morse), A., i, 606.
- **Stachydrin** from lucerne hay (Steenbock), A., i, 439.
- **Stains** for microscopic work, derived from methylene-blue (Tribondeau and Dubreuil), A., i, 285.
- **Stannic** salts. See under Tin.
- **Starch**, stability of solution of (Pollitz), A., ii, 499.
  - formation of, by moulds (Boas), A., i, 370.
  - formation of, in plants exposed to light of various sources (Ursprung), A., i, 504.
  - determination of the gelatinisation temperature of (Dox and Roark), A., ii, 276.
  - autolysis of (Biedermann), A., i, 62.
  - action of formaldehyde on (Woker), A., i, 61, 447; (v. Kaufmann), A., i, 251; (Maggi and Woker), A., i, 686.
  - hydrolysis of, by malt amylase (Sherman and Walker), A., i, 597.
  - digestion of various forms of, with diastase (Pauletig), A., i, 670.
  - effect of soaps on the diastatic fermentation of (Kende), A., i, 615.
  - estimation of (v. Fellenberg), A., ii, 342.
  - estimation of, polarimetrically (Baumann and Grossfeld), A., ii, 223.
  - estimation of, in clover (v. Fellenberg), A., ii, 515.
- **Stars**, ozone in the spectra of (Fowler and Strutt), A., ii, 522.
- **Stas**, work of (*Scott*), T., 288.
- **Staurolite** (Hörner; Wülfing and Hörner), A., ii, 325.
- **Stearic acid**, *p*-nitrobenzyl ester (Lyons and Reid), A., i, 559.
  - estimation of, in butter fat (Holland, Reed, and Buckley), A., ii, 50.
- **Stearo-*p*-ethoxyanilide** (de' Conno), A., i, 388.
- **Stearo-*p*-hydroxyanilide** (de' Conno), A., i, 387.
- **Stearo-*p*-methoxyanilide** (de' Conno), A., i, 388.
- **Stearo-α- and -β-naphthalides** (de' Conno), A., i, 388.
- **Stearo-*p*-phenylenediamide** (de' Conno), A., i, 389.
- **Stearo-*p*-toluidide** (de' Conno), A., i, 387.
- **Steel.** See under Iron.

Stereochemical studies (Holmberg), A., i, 115.

Stereochemistry of crystals (Rinne), A., ii, 18.

Stereoisomeric compounds, surface tension of (Berczeller), A., ii, 442.

Stibiobismuthinite (Koenig), A., ii, 487.

Stilbene, and 2:4:6-*tri*nitro-, additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 207.

Stilbene, *αα*-*di*bromo-2:2′-*di*amino- (Ruggli), A., i, 587.

4:4′-*di*fluoro-, and -*di*iodo- (Meyer and Hofmann), A., i, 642.

4-nitro-2-cyano-4′-hydroxy-, and its acetyl derivative (Pfeiffer, Klinkert, and v. Pollitzer), A., i, 140.

Stilbite from Hungary (Vendl), A., ii, 493.

Still, for use with ether (Smith and Morgan), A., ii, 28.

Strontium alloys with mercury and sodium, equilibrium of sodium and strontium chlorides with (Smith and Braley), A., ii, 455.

Strontium chloride, double salt of cæsium chloride and (Jamieson), A., ii, 139.

equilibrium of solutions of sodium chloride and, with amalgams of sodium and strontium (Smith and Braley), A., ii, 455.

Strontium, estimation of, in water (Averitt), A., ii, 423.

Strychnine, compound of mercuric nitrite and (Rây), T., 508; A., i, 470.

estimation of, in nux vomica (Jensen), A, ii, 56.

2-Styrylbenziminazoles, amino-, nitro-, and hydroxy-, and their derivatives (Kym and Jurkowski), A., i, 176.

Styryl cinnamylidenemethyl ketone, additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 208.

6-Styryl-2:4-diphenylpyryl ferrichloride (Dilthey), A., i, 661.

Styryl methoxycinnamylidenemethyl ketones, and their derivatives (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, *209.

Styryl *p*-methoxystyryl ketone, additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 208.

Styryl methylenedioxycinnamylidenemethyl ketone, additive compound of perchloric acid and (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 209.

Substance, $C_2H_4N_2S$, from formaldehyde and thiocarbamide (Dixon and Taylor), A., i, 12.

$C_3H_6N_2S$, from acetaldehyde and thiocarbamide (Dixon and Taylor), A., i, 11.

$C_3H_8N_4S_2$, from methylene di-iodide and thiocarbamide (Dixon and Taylor), A., i, 12.

$C_3H_7O_2NCl_2$, from carbonyl chloride and *α*-ethoxyammonium chloride (Jones and Neuffer), A., i, 325.

$C_5H_8O_2N_2S$, from carbomethoxythiocarbimide and aldehyde-ammonia (Dixon and Taylor), A., i, 12.

$C_5H_{13}O_3N_2Cl$, from carbonyl chloride and ethoxyamine (Jones and Neuffer), A., i, 325.

$C_6H_{10}O_2N_2S$, from carbethoxythiocarbimide and aldehyde-ammonia (Dixon and Taylor), A., i, 12.

C_8H_7ON, from *p*-benzoquinone and acetaldehyde-ammonia (Ghosh), T., 611; A., i, 518.

C_8H_9ON, from pyrrole-2-aldehyde and acetone (Lubrzynska), A., i, 53.

$C_8H_{15}O_5N$, from ethyl bromoacetate and hydroxylamine (Jones and Werner), A., i, 381.

$C_8H_9O_2NCl_2$, from carbonyl chloride and *α*-benzyloxyammonium chloride (Jones and Neuffer), A., i, 325.

$C_9H_{16}O_7$, from trimethyl glucose and hydrocyanic acid (Denham and Woodhouse), T., 248.

$C_9H_{11}ON$, from pyrrole-2-aldehyde and methyl ethyl ketone (Lubrzynska), A., i, 53.

$C_{12}H_8O_3N_2$, from 3:3′-diphenol and nitrous acid (Borsche), A., i, 558.

$C_{13}H_{11}ON$, from pyrrole-2-aldehyde and acetophenone (Lubrzynska), A., i, 53.

$C_{15}H_{10}O_8N_4$, from trinitroacetylaminophenol and aminosalicylic acid (Meldola, Foster, and Brightman), T., 538; A., i, 453.

$C_{16}H_{16}O_4N_2$, from phenylhydrazine and opianic acid (Mitter and Sen), T., 991.

$C_{18}H_{12}O_2$, from anthraquinone and acetaldehyde-ammonia (Ghosh), T., 611; A., i, 518.

$C_{20}H_{26}N_2$, from *cyclo*hexanone and pyrrole (Tschelincev, Tronov, and Karmonov), A., i, 412.

$C_{25}H_{32}N_4$, from acetone and pyrrole (Tschelincev and Tronov), A., i, 92.

$C_{28}H_{25}O_2N$, and its salts, from methyl *p*-dimethylamino-*o*-benzoylbenzoate and magnesium phenyl bromide (Pérard), A., i, 651.

Substance, $C_{29}H_{26}O_4$, from greenheart wood (Oesterle), A., i, 505.
  $C_{30}H_{40}N_4$, from pyrrole, acetone and methyl ethyl ketone (Tschelincev and Tronov), A., i, 412.
  $C_{32}H_{44}N_4$, from pyrrole and methyl ethyl ketone (Tschelincev and Tronov), A., i, 411.
  $C_{34}H_{44}N_4$, from pyrrole, acetone and *cyclo*hexanone (Tschelincev, Tronov, and Karmanov), A., i, 413.
  $C_{48}H_{76}N_4$, from pyrrole and methyl hexyl ketone (Tschelincev and Tronov), A., i, 412.
  $C_{84}H_{108}O_3N_{12}$, from acetone and pyrrole (Tschelincev and Tronov), A., i, 92.
i-**Succinamic acid**, β-iodo- (Kallenberg), A., i, 279.
Succinic acid, preparation of, by oxidation of alkali butyrates (Cahen and Hurtley), A., i, 535.
  physiological oxidation of (Westerlund), A., i, 68.
  and bromo-, *p*-nitrobenzyl esters (Lyman and Reid), A., i, 334.
  estimation of (Grey), A., ii, 517.
Succinic acid, bromo-, action of sodium methoxide with (Madsen), A., ii, 250.
Succinic acids and their homologues and derivatives, crystallography of (Steel), A., i, 535.
  halogen-substituted, action of potassium xanthate on salts of (Holmberg), A., i, 115.
*cyclo***Succinyl***di***aminotolane**, constitution of (Ruggli), A., i, 22.
Succinylsuccinic acid, ethyl ester, keto-enol isomerism of (Hantzsch), A., i, 685.
Sucrose (*saccharose: cane-sugar*), structure of (Haworth and Law), A., i, 80.
  action of acids on rotation of, in presence of soluble salts (Saillard and Wehrung), A., i, 513.
  influence of pressure on the velocity of inversion of (Cohen and Valeton), A., ii, 566.
  inversion of, by hydrochloric acid (Waterman), A., i, 631.
  effect of methyl acetate on the inversion of (Griffith, Lamble, and Lewis), T., 390; A., ii, 302.
  adsorption of (Rakuzin), A., ii, 294.
  resorption of, in the body (Brahm), A., i, 428.
  action of formaldehyde on (Heiduschka and Zirkel), A., i, 446.
  estimation of (Müller), A., ii, 222.
  estimation of, in molasses (Staněk), A., ii, 342.
Sucrose (*saccharose: cane-sugar*), estimation of, polarimetrically (Walker), A., ii, 395.
Sucrose phosphoric acid, fermentation of (Djenab and Neuberg), A., i, 680.
Sugar, formation of, in the animal organism (Cremer, Seuffert, Berger, Pape, and Fabische), A., i, 240.
  formation of, in the liver (Baldes and Silberstein), A., i, 673.
  assimilation and fermentation of (Bokorny), A., i, 681.
  in blood (McDanell and Underhill), A., i, 359.
    nature of (McGuigan), A., i, 359.
  estimation of, filter tube for (Boericke), A., ii, 547.
  estimation of, in blood (Rainy and Hawick), A., ii, 49; (Wolf and Ball), A., ii, 106; (McGuigan), A., ii, 428.
  in blood and urine, estimation of (Cammidge), A., ii, 276.
  estimation of, in meat extracts (Smith), A., ii, 49.
  estimation of, in urine (Myers), A., ii, 221; (Vanino and Bertele), A., ii, 342; (Sidersky), A., ii, 548; (Ruoss), A., ii, 549; (Lenk), A., ii, 555.
  invert-. See Invert-sugar.
Sugars, mutarotation of (Hudson and Yanovsky), A., i, 445.
  rotation and cryoscopic behaviour of, in formamide and in water (Mackenzie and Ghosh), A., i, 79.
  polarisation of solutions of, without treatment with acetates (Pellet), A., ii, 428.
  precipitation of reducing substances from impure solutions of, by lead acetate (Pellet), A., i, 8.
  sublimation of (Ghosh), A., i, 80.
  degradation of (Weerman), A., i, 546.
  origin of nitrogenous pigments in the products from refining (Staněk), A., i, 544.
  preparation of the bromoacetyl derivatives of (Dale), A., i, 7.
  action of diphenylmethanedimethyldihydrazine with (v. Braun), A., i, 251.
  reducing, action of amino-acids on (Maillard), A., i, 251.
    estimation of (Schoorl and Regenbogen; Pellet), A., ii, 222.
  analysis of (Rolle), A., ii, 104.
  analysis of foods containing (Lajoux and Ronnet), A., ii, 582.

Sugars, fluorescent reaction to distinguish (Guglialmelli), A., ii, 276.
estimation of (Wolf; López; Schoorl and Kolthoff), A., ii, 514.
estimation of, in blood (Feigl), A., i, 64.
Sulphamidobenzoic acid, azide and hydrazide of, and their derivatives (Schrader), A., i, 709.
Sulphanilic acid, 3-nitro-, preparation of (Farbenfabriken vorm. F. Bayer & Co.), A., i, 87.
Sulphide, $C_6H_{12}S$, and its derivatives, from 2-methyltetrahydrothiophen (Grischkevitsch-Trochimovski), A., i, 158.
$C_7H_{14}S$, and its methiodide, from 2-methylpentamethylene sulphide (Grischkevitsch-Trochimovski), A., i, 158.
Sulphides, dissociation pressure of (Allen and Lombard), A., ii, 194.
action of, on metallic silver (Hahn), A., ii, 371.
cyclic, properties and reactions of (Grischkevitsch-Trochimovski), A., i, 158.
decomposition of (Grischkevitsch-Trochimovski), A., i, 157.
estimation of, in ores (Scheidler), A., ii, 503.
Sulphinic acids, aromatic, action of di- and tri-phenylcarbinols with (Hinsberg), A., i, 328.
Sulphites. See under Sulphur.
Sulphocarboxylic acids, azides and hydrazides of (Schrader), A., i, 709.
p-**Sulphomethylaminophenylarsinic acid** (Abelin), A., i, 487.
Sulphonephthaleins, use of, as indicators (Lubs and Acree), A., ii, 97.
Sulphonic acids, amino-, displacement of sulphonic acid groups in, by halogens (Sudborough and Lakhumalani), T., 41; A., i, 128.
Sulphonylbenzoic acid, *o*-amino-. See Sulphamidobenzoic acid.
Sulphonylphenyl-1:3:4-triazole, 2:5-*di*-*o*-amino-, and 1-amino-2:5-*di*-*o*-amino- (Schrader), A., i, 709.
δ-Sulpho-δ-phenyl-Δ$^{\alpha}$-pentenoic acid, and *α*-bromo-, and their derivatives (Nottbohm), A., i, 28.
Sulphur, atomic weight of (Moles; Guye), A., ii, 257.
black (Neumann), A., ii, 464.
colloidal, formation of, from sulphides (Dittler), A., ii, 443.
absorption of light by solutions of (Pihlblad), A., ii, 557.
in soils, effect of lime and magnesia on (MacIntire, Willis, and Holding), A., i, 723.
Sulphur metabolism. See Metabolism.
action of, on naphthenes (Friedmann), A., i, 13.
apparatus for extraction of, from arsenic trisulphide (v. Spallart), A., ii, 102.
Sulphur compounds in urine (Salkowski), A., i, 304.
estimation of, in lime-sulphur liquids (Wöber), A., ii, 503.
estimation of, in urine (Weiss), A., ii, 217.
Sulphur chloride, action of, on metals (Domanicki), A., ii, 369.
*di*oxide, adsorption of, by charcoal (Williams), A., ii, 362.
action of, on metallic oxides (Hammick), T., 379; A., ii, 306.
reactions between ammonia, ammonium thiosulphate, and polythionate and (Espenhahn), A., ii, 310.
estimation of (Sweeney, Outcault, and Withrow), A., ii, 577.
estimation of, iodometrically (Ferguson), A., ii, 267.
Sulphurous acid, preparation of (Hart), A., ii, 256.
electrolytic oxidation of (M. de K. and N. J. Thompson), A., ii, 137.
Sulphites, velocity of reaction of iodates with (Eggert), A., ii, 197.
estimation of, iodometrically (Ferguson), A., ii, 267.
Sulphuric acid, optical investigation of mixtures of nitric acid and (Schaefer and Niggemann), A., ii, 186.
ionisation of (Müller), A., ii, 117.
adsorption of, by ferric hydroxide (Dittler), A., ii, 443.
distillation of mixtures of nitric acid, water and (Pascal), A., ii, 569.
purification of, from nitric acid (Steenbergen), A., ii, 421.
reaction of ethyl alcohol with (Evans and Albertson; Kremann), A., i, 314.
action of hydrogen on (Jones), A., ii, 530.
action of, on nitrobenzene (Crossley and Ogilvie), A., i, 328.
titration of (Gyzander), A., ii, 39.
detection of arsenic in (Kling), A., ii, 579.
free, detection and estimation of, in presence of sulphates (Vulquin and Entat), A., ii, 268.
rapid estimation of (Richmond and Merreywether), A., ii, 503.
estimation of, in presence of nitric and picric acids (Richardson), A., ii, 158.

Sulphur:—
Sulphuric acid, estimation of arsenic in (Pérégrin), A., ii, 180.
fuming, estimation of free sulphur trioxide in (Parker), A., ii, 420.
Sulphates, formation of double nitrates and (Massink), A., ii, 412.
precipitation of, by barium chloride, in presence of iron (Smith), A., ii, 371.
distribution of, between corpuscles and plasma in blood (de Boer), A., i, 671.
Persulphates, detection of, in presence of other per-salts (Monnier), A., ii, 98.
Thiosulphates, estimation of, volumetrically, with iodine (Kempf), A., ii, 502.
Hyposulphites, use of, in gas analysis, to replace pyrogallol (Descamps), A., ii, 216.
Sulphur organic compounds:—
Sulphurous acid, aryl esters of (Richter), A., i, 24.
action of pyridine and of piperidine on (Raffo and Balduzzi), A., i, 382.
Sulphur detection and estimation:—
detection of, microchemically (Emich), A., ii, 218.
estimation of, in iron and steel (Pulsifer), A., ii, 100.
estimation of, in roasted ores (Pérégrin), A., ii, 179.
estimation of, in organic compounds (Merl and Lüft), A., ii, 383.
detection and estimation of, in petroleum (Francis and Crawford), A., ii, 379.
estimation of, in pyrites (Zay), A., ii, 328; (Phillips), A., ii, 379; (Craig), A., ii, 420.
estimation of, in vulcanised rubber (Eaton and Day), A., ii, 150.
estimation of, in urine (Givens), A., ii, 180.
Sulphuric and **Sulphurous acids**. See under Sulphur.
Sun, ozone in the spectrum of (Fowler and Strutt), A., ii, 522.
Supercooling and capillarity (Bigelow and Rykenboer), A., ii, 444.
Superphosphates. See under Phosphates.
Surface tension (Harkins, Brown, and Davies), A., ii, 238; (Harkins, Davies, and Clark), A., ii, 239.
measurement of, by means of drop weights (Perrot), A., ii, 408.
determination of, by means of vortex rings (Kutter), A., ii, 69.
Surface tension, tables of (Somogyi), A., ii, 124.
of liquids (Jaeger and Kahn), A., ii, 69, 70, 71.
of mixed liquids (Morgan and Evans), A., ii, 561.
of metals and alloys (Smith), A., ii, 408.
of stereoisomeric compounds (Berczeller), A., ii, 442.
Swelling of substances in contact with water (Katz), A., ii, 245.
Swine, effect of wheat on the growth and development of (McCollum, Simmonds, and Pitz), A., i, 184.
Systems, containing many components (Eitel), A., ii, 565.

T.

Tanning, theories of (Procter and Wilson), A., i, 91.
Tannins, detection of, in plant tissues (Sperlich), A., ii, 400.
Tantalum chloride, stability of, and its use in atomic weight determinations (Sears), A., ii, 481.
Tantalum, estimation of, in steel (Kelley, Myers, and Illingworth), A., ii, 546.
Tapiolite from Western Australia (Simpson), A., ii, 377.
Tar, vacuum, alcohols and bases of (Pictet, Kaiser, and Labouchère), A., i, 515.
Tartaric acid, sterical relationship of glyceraldehyde and (Wohl and Momber), A., i, 319.
calcium salt, crystallisation of (Chattaway), A., i, 4.
cinnamates of (Erlenmeyer and Hilgendorff), A., i, 26.
esters, rotation of (Patterson), A., ii, 3, 4, 5.
metallic and amine esters, rotatory power of (Casale), A., i, 378.
p-nitrobenzyl ester (Reid), A., i, 334.
amides and imides of (Casale), A., i, 545, 643.
azide and hydrazides of, and their derivatives (Curtius and Ohlgart), A., i, 638.
detection of (Broeksmit), A., ii, 429.
estimation of, in presence of calcium tartrate (Carles), A., ii, 278.
Tartranilic acid. See Phenyltartramic acid.
Teeth, estimation of selenium in (Gassmann), A., ii, 540.
Telephone receiver, use of, as an indicator in electrical conductivity measurements (Washburn and Parker), A., ii, 235.

Tellurium, atomic weight of (Stahler and Tesch), A., ii, 202.

Tellurium alloys with silver (Chikashige and Saito), A., ii, 139.

Tellurium *per*chlorate (Fichter and Schmid), A., ii, 203.

Telluric acid, reduction of (Benger), A., ii, 569.

methyl ester (Pellini), A., i, 2.

Tellurium organic compounds (Lederer), A., i, 134.

Temperature, critical. See Critical.

high, reactions at (Lewis), T., 1086; (Ruff and Jellinek), A., ii, 92; (Ruff and Lauschke), A., ii, 95.

Terephthalic acid, *p*-nitrobenzyl ester (Lyons and Reid), A., i, 559.

Terephthalic acid, *p*-*di*hydroxy-, ethyl ester, keto-enol isomerism of (Hantzsch), A., i, 685.

Terephthaylidenedicyanoacetic acid, ethyl ester (Kauffmann and Jeutter), A., i, 395.

Terephthaylidenedicyanoacetophenone (Kauffmann and Jeutter), A., i, 395.

Terephthalylidenedi-indandione (Kauffmann and Jeutter), A., i, 395.

Terephthalylidenedimalononitrile (Kauffmann and Jeutter), A., i, 395.

n- and *iso*-**Teresantalic acids**, and their salts and derivatives (Rupe and Tomi), A., i, 138.

Terpenes, aliphatic (Enklaar), A., i, 111, 377.

action of ozone on (Harries and Neresheimer), A., i, 211.

Terpin, crystallographic constants of (Rose), A., ii, 257.

Terpineol, hydration of, with acids (Prins), A., i, 518.

Tethelin, influence of, on growth of white mice (Robertson and Drummond), A., i, 673.

Tetra-acetylglucosidoglycollonitrile (Fischer and Bergmann), A., i, 658.

Tetra-acetylglucosidomandelic acid, ethyl esters and amides of (Fischer and Bergmann), A., i, 658.

Tetra-anisylideneaminodiphenyl-*p*-azophenylene (Heiduschka and Goldstein), A., i, 484.

Tetrabenzylideneaminodiphenyl-*p*-azophenylene (Heiduschka and Goldstein), A., i, 484.

Tetra-*p*-chlorobenzylideneaminodiphenyl-*p*-azophenylene (Heiduschka and Goldstein), A., i, 484.

Tetracinnamylideneaminodiphenyl-*p*-azophenylene (Heiduschka and Goldstein), A., i, 484.

Tetraethyl*hexa*aminoarsenobenzene hydrochloride (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 359.

Tetraethylammonium palladichloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 542.

palladotribromide (Gutbier and Fellner), A., i, 542.

silicate (Schwarz), A., ii, 32.

Tetraethylhydrindacenes (Freund, Fleischer, and Gofferjé), A., i, 574.

Tetraethylhydrindacene-1:3-diones (Freund, Fleischer, and Gofferjé), A., i, 574.

d-**Tetragalacturonic acid** (Ehrlich), A., i, 322.

Tetrahydrofurandicarbamic acid, *di*hydroxy-, silver salt (Curtius and Darapsky), A., i, 638.

Tetrahydrofurandicarbamo-γ-dilactone, *di*hydroxy- (Curtius and Darapsky), A., i, 638.

Tetrahydrothebainone, hydroxy-, and its methiodide (Freund and Speyer), A., i, 219.

"**Tetrahydrothebaone**," 7-hydroxy- (Freund and Speyer), A., i, 219.

Tetrahydrothiophen, preparation of, and its derivatives (Grischkevitsch-Trochimovski), A., i, 154.

Tetramethoxyacetophenone (Nierenstein), T., 7; A., i, 150.

2:3:4:6-Tetramethoxybenzoic acid, and its derivatives (Nierenstein), T., 6; A., i, 150.

2:2′.4:4′-Tetramethoxydiphenylmethane (Pfeiffer and Grimmer), A., i, 662.

6:7:6′:7′-Tetramethoxyindigotin, 4:4′- and 7:7′-*di*bromo- (Jones and Robinson), T., 921.

3:6-Tetramethyl*di*amino-9-*p*-hydroxyphenylxanthene, and its benzoyl derivative (Ghosh and Watson), T., 827.

Tetramethyl*di*aminophenazine (Karrer, Kehrmann, and Falconnier), A., i, 356.

Tetramethyl*di*aminodiphenylmethyl β-anthraquinonyl sulphone (Hinsberg), A., i, 329.

4′:4′-Tetramethyl*di*aminotriphenylcarbinol. See Malachite-green.

Tetramethyl*hexa*aminoarsenobenzene hydrochloride (Farbwerke vorm. Meister, Lucius, & Brüning), A., i, 359.

Tetramethylammonium iodide, crystalline structure of (Vegard), A., ii, 296.

palladichloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 542.

Tetramethylammonium palladochloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.
2:3:5:7-Tetramethylbenzo-γ-pyrone, preparation of, and its salts and derivatives (Simonis and Herovici), A., i, 580.
2:4′-Tetramethyldiaminophenyl *m*-**tolyl ketone** (v. Braun), A., i, 175.
Tetramethylorcinol, derivatives of (Herzig and Wenzel), A., i, 133.
Tetramethylurinoporphyrin, *tetra*chloro-, dihydrochloride (Fischer), A., i, 713.
Tetraphenylethane, synthesis of (Scharvin and Plachuta), A., i, 179.
Tetraphenylfuran, 3:4-*di*-*p*-nitro- (Francis), T., 1039.
Tetraphenylmethane, preparation of (Gomberg and Kamm), A., i, 642.
Tetraphenylmethane-*o*-carboxylic acid, and its salts (Copisarow), T., 17; A., i, 145.
Tetrapiperonylideneaminodiphenyl-*p*-azophenylene (Heiduschka and Goldstein), A., i, 484.
Tetravanillylideneaminodiphenyl-*p*-azophenylene (Heiduschka and Goldstein), A., i, 484.
Thalleioquinine (Christensen), A., i, 51.
Thallium salts, effect of, on lactic fermentation (Richet), A., i, 370.
Thallium borate, crystal structure of (Scharizer), A., ii, 473.
Thallous fulminate (Wöhler and Martin), A., i, 383.
Thallium ammines (Ephraim and Millmann), A., ii, 320.
Thaumasite from New Jersey (Brown), A., ii, 146.
Thebaine (Freund and Speyer), A., i, 217.
Thebainone, hydroxy-, and its derivatives (Freund and Speyer), A., i, 218.
Theobromine, estimation of (Débourdeaux), A., ii, 348; (Radford), A., ii, 519.
estimation of, in cacao and chocolate (Savini), A., ii, 109.
Thermal properties, relation between chemical constitution and, of organic compounds (Pagliani), A., ii, 120.
diffusion, separation of gases by (Chapman), A., ii, 444.
dissociation of alkali haloids (Ephraim), A., ii, 531.
Thermochemistry, use of sodium peroxide in (Mixter), A., ii, 123.
Thermo-element, copper-constantan (Richards and Richter), A., ii, 232.
Thermometer, stem correction of (Wheeler), A., ii, 65.
Thermostat for use with a polarimeter (Paul), A., ii, 5.
Thienyl*di*chloroarsine (Steinkopf and Bauermeister), A., i, 303.
Thienyl ketones, preparation of (Steinkopf), A., i, 278.
Thiocarbamide, salts of (Dixon), T., 684; A., i, 545.
compounds of alkyl esters with (Taylor), T., 650; A., i, 514.
action of acetic anhydride on, and its potassium derivative (Werner), A., i, 11.
compound of antimony trichloride and (Vanino and Mussgnug), A., i, 196.
formation of guanidine from (Schmidt), A., i, 449.
Thiocarbamides, interaction of aldehydes and (Dixon and Taylor), A., i, 11.
compounds of bismuth haloids with (Vanino and Mussgnug), A., i, 197.
compounds of mercuric nitrite and (Rây), T., 106; A., i, 194.
Thiocyanic acid, formation of, in animals (Dezani), A., i, 676.
ammonium salt, condensation of formaldehyde with (Schmerda), A., i, 545.
Thiocyanates, detection of (Curtman and Harris), A., ii, 108.
Thionaphthen, *tetra*bromo- (Meyer and Wesche), A., i, 313.
Thiophen-mercurihaloids and their halogen derivatives (Steinkopf), A., i, 302.
Thiotolen, *tetra*bromo- (Meyer and Wesche), A., i, 313.
Thorium, charged condition of the active deposits of (Henderson), A., ii, 351.
Thrombin, investigations with (Resch), A., i, 303.
in blood (Gasser), A., i, 426.
Thuringite from Colorado (Larsen and Steiger), A., ii, 148.
Thymine-nucleoside (Johnson and Hadley), A., i, 667.
Thymol, solubility of, in mixtures of water and glycerol (Marquina), A., i, 689.
estimation of (Elion), A., ii, 514.
Thymolphthalein, use of, in colorimetric analysis (Moir), A., ii, 386.
Thymyl *p*-nitrobenzyl ether (Reid), A., i, 333.
sulphite (Richter), A., i, 24.
Thyroid, active constituent of (Kendall), A., i, 364.

Tin, electrode potentials of lead and (NOYES and TOABE), A., ii, 458.
Tin alloys with bismuth and with cadmium (BUCHER), A., ii, 211.
Tin salts, inhibition of digestion of proteins by absorbed (GOSS), A., i, 497.
  Stannic chloride, viscosity of systems formed by, with benzene or esters (KURNAKOV, PERLMUTTER, and KANOV), A., ii, 360; (KURNAKOV and BEKETOV), A., ii, 361.
    additive compounds of (PFEIFFER. JOWLEFF, FISCHER, MONTI, and MULLY), A., i, 208.
Tin estimation and separation:—
  electroanalysis of (BATUECAS), A., ii, 106.
  estimation of, volumetrically (HALLETT), A., ii, 46.
  estimation of, in alloys (HAGMAIER), A., ii, 181.
  estimation of, in tin-plate (KOLTHOFF and VAN LOHUIZEN), A., ii, 426.
  estimation of, and its separation from antimony (PRIM), A., ii, 392.
  separation of tungsten and (TRAVERS), A., ii, 545.
Tin plate, detinning and analysis of (HEISE and CLEMENTE), A., ii, 337.
  estimation of tin in (KOLTHOFF and VAN LOHUIZEN), A., ii, 426.
Tissues, animal. See Animal tissues.
  chemical individuality of the elements of (LEVENE), A., i, 363.
  muscular, glycolytic properties of (HOAGLAND and MANSFIELD), A., i, 674.
    urea in (HOAGLAND and MANSFIELD), A., i, 674.
  detection of arsenic in (GAUTIER and CLAUSMANN), A., ii, 421.
Titanium, pure, preparation of (PODSZUS), A., ii, 373.
  *tri*chloride, use of, in analysis (MACH and LEDERLE), A., ii, 580.
  *di*oxide, equilibrium of carbon dioxide and (NIGGLI), A., ii, 211.
Titration flask (BEZZENBERGER), A., ii, 499.
Tobacco, biochemistry of (PARIS), A., ii, 227.
  estimation of nicotine in (TINGLE and FERGUSON), A., ii, 55; (THOMSEN), A., ii, 431.
Tolane, *o'*-nitro-*o*-amino-, and *oo'*-*di*nitro-, and their derivatives (RUGGLI), A., i, 22.
Toluene, heat of combustion of (RICHARDS and DAVIS), A., ii, 237.
  action of, on fermentation (BUCHNER and SKRAUP), A., i, 613.

Toluene compounds, Me = 1.

Toluene, effect of, on the olfactory organ (BACKMAN), A., i, 198.
  electrochemical chlorination of (FICHTER and GLANTZSTEIN), A., i, 124.
  additive compounds of (PFEIFFER, JOWLEFF, FISCHER, MONTI, and MULLY), A., i, 207.
  estimation of, in coal tar oil (HARKER), A., ii, 338.
  separation of benzene, xylene and, from light oils (EGLOFF), A., ii, 338.
Toluene, bromo-, chloro-, and iodonitro-, and nitro- (KÖRNER and CONTARDI), A., i, 86.
  o-chloro-, preparation of (BADISCHE ANILIN- & SODA-FABRIK), A., i, 258.
  o-iodo-, oxidation of, with potassium permanganate (MONTAGNE), A., i, 84.
  nitro-, estimation of (COLVER and PRIDEAUX), A., ii, 340, 512; (KNECHT), A., ii, 427.
  2:3:6-*tri*nitro-, and its derivatives (KÖRNER and CONTARDI), A., i, 85.
  2:4:6-*tri*nitro-, preparation of (HUMPHREY), A., i, 18.
Tolueneazo-α-naphthalenediazosulphonic acids, potassium salts (TRÖGER and LANGE), A., i, 418.
Tolueneazo-α-naphthylamines, and their salts (TRÖGER and LANGE), A., i, 418.
Tolueneazo-α-naphthylanisylidenehydrazines (TRÖGER and LANGE), A., i, 418.
Tolueneazo-α-naphthylcinnamylidenehydrazines (TRÖGER and LANGE), A., i, 418.
Tolueneazo-α-naphthylhydrazinesulphonic acids, potassium salts (TRÖGER and LANGE), A., i, 418.
Tolueneazo-α-naphthylsalicylidenehydrazines (TRÖGER and LANGE), A., i, 418.
Tolueneazo-α-naphthyl-*p*-tolylidenehydrazines (TRÖGER and LANGE), A., i, 418.
p-**Toluenesulphonic acid**, phenyl esters, and their derivatives (BAUDISCH and KARZEFF), A., i, 331.
1-*p*-Toluenesulphonylamino-4-methoxy-2-methylthioxanthone (ULLMANN and V. GLENCK), A., i, 161.
1-*p*-Toluenesulphonylamino-4-methylthioxanthone (ULLMANN and V. GLENCK), A., i, 160.
o-**Toluic acid**, *p*-nitrobenzyl ester (REID), A., i, 333.

Toluene compounds, Me = 1.
m-**Toluic acid,** *p*-nitrobenzyl ester (Lyman and Reid), A., i, 334.
p-**Toluic acid,** and *p*-thiol-, *p*-nitrobenzyl esters (Lyons and Reid), A., i, 559.
Toluic acids, *o*- and *p*-thiol-, and their esters (Sachs and Reid), A., i, 87.
o-**Toluidine,** condensation of formaldehyde with (Kroneberg), A., i, 170.
  additive compound of, with 2:4:6-trinitrostilbene (Pfeiffer, Jowleff, Fischer, Monti, and Mully), A., i, 208.
4-Toluidine, bromonitro-, and nitro- (Körner and Contardi), A., i, 86.
  2:6-*di*nitro-, polymorphism of (Artini), A., i, 389.
1-*p*-Toluidino-4-methylthioxanthone (Ullmann and v. Glenck), A., i, 160.
β-Toluidino-β-phenylethyl ethyl ketones (Mayer), A., i, 89.
β-*p*-Toluidino-β-phenylethyl hexyl ketone (Mayer), A., i, 90.
β-*m*-Toluidino-β-phenylethyl nonyl ketone (Mayer), A., i, 90.
β-*p*-Toluidino-β-phenylethyl styryl ketone (Mayer), A., i, 144.
3-*p*-Toluidino-5-phenyl*iso*oxazole (Worrall), A., i, 336.
p-**Toluidinoveratrole,** *di*nitro- (Hindmarsh, Knight, and Robinson), T., 946.
p-**Toluoylphenylethylene oxide,** and its diacetate (Jörlander), A., i, 345.
4-*o*- and -*p*-Toluoyl-1-phenyl-3-methylpyrazoles, 5-chloro- (Michaelis and Rojahn), A., i, 480.
Tolyl *p*-nitrobenzyl ethers (Reid), A., i, 333.
p-**Tolyl** carbonate, nitration of (Holleman and Hoeflake), A., i, 133.
o-, *m*-, and *p*-**Tolyl** sulphites (Richter), A., i, 24.
p-**Tolyl*iso*amylparabanic acid** (Stieger), A., i, 172.
p-**Tolyl*iso*amylthiocarbamide** (Stieger), A., i, 172.
p-**Tolyl*iso*amylthioparabanic acid** (Stieger), A., i, 172.
3-*p*-Tolyl-2-benzylquinoxaline (Jörlander), A., i, 345.
β-*p*-Tolylbutane, αα-*di*chloro- (v. Auwers), A., i, 34.
o-**Tolylcarbamide,** 4-amino-, and its derivatives (Jacobs and Heidelberger), A., i, 584.
p-**Tolylcinnamic acid,** ethyl ester, action of sodium benzyl cyanide with (Daughters), A., i, 647.

Toluene compounds, Me = 1.
3-*o*-Tolyl-5:5-dimethylhydantoin, and its derivatives and 2-thio- (Bailey and McPherson), A., i, 54.
2:4-Tolylenediammonium palladochloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.
s-*p*-**Tolylethoxymethylcarbamide** (Curtius and van der Laan), A., i, 636.
o-**Tolylethylnitroamine,** 3:4:5-*tri*nitro- (Jansen), A., i, 129.
p-**Tolylethylnitrosoamine,** 2:5-*di*nitro- (Jansen), A., i, 129.
3-Tolyl-5-*op*-*di*hydroxybenzylidenerhodanine (Andreasch), A., i, 663.
p-**Tolyl ω-hydroxystyryl ketone** (Jörlander), A., i, 345.
p-**Tolylideneazobenzene-*p*-hydrazone** salts (Tröger and Piotrowski), A., i, 668.
m-**Tolylmalonic acid,** 6-nitro-4-cyano-, methyl ester (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 17.
p-**Tolyl methyl ketone,** 3-chloro- and 3-chloro-6-nitro-, and their derivatives (Borsche, Stackmann, and Makaroff-Semljanski), A., i, 18.
α-*p*-Tolyl-α-methylpropaldehyde, and its derivatives (v. Auwers), A., i, 35.
α-*p*-Tolyl-β-methylpropan-αβ-diol (v. Auwers), A., i, 35.
β-*o*-Tolylpropionic acid, β-bromo- (v. Auwers), A., i, 267.
Tolylsulphone, *p*-hydroxy-, and its salts and derivatives (Zehenter), A., i, 134.
1-*p*-Tolyl-5-styryl-Δ^1-*cyclo*hexen-3-one, and its semicarbazone (Scholtz), A., i, 463.
Tolylthiocarbimides, condensation of sodiophenylacetylene with (Worrall), A., i, 335.
m-**Tolylthiolbenzoic acid,** 2-*p*-chloro- (Ullmann and v. Glenck), A., i, 160.
Torula, red, colouring matter extracted from (Chapman), A., i, 244.
Tourmaline, composition of (Boeke), A., ii, 178.
  from Renfrew, Ontario (Bruce), A. ,ii, 378.
Toxicity, relation between valency and (Friedberger and Joachimoglu), A., i, 306.
Toxins, optical activity of (Rakuzin), A., ii, 286.
  adsorption of, and antitoxins by aluminium hydroxide (Rakuzin and Flier), A., i, 181.
Transformation, spontaneous, direction of (Tancov), A., ii, 367.

Transport numbers, dependence of, on the nature of the solvent (Krüger), A., ii, 118.

Trees, forest, constituents of the leaves of (Serex), A., i, 505.

*iso*Trehalose, thio-, and its derivatives (Schneider and Wrede), A., i, 540.

Tri*iso*amylammonium palladi- and pallado-chlorides (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.

2:4:6-Trianisylpyran oxide (Dilthey), A., i, 579.

2:4:6-Trianisylpyryl salts (Dilthey), A., i, 579.

Triarylmethyls, molecular weights of (Gomberg and Schoepfle), A., i, 551.

Triarylmethylazides, molecular rearrangement of (Senior), A., i, 97.

Tribenzoylchrysophanic acid (Eder), A., i, 465.

Tribenzoylemodinanthranol methyl ether (Eder), A., i, 465.

Tribenzoylphrenosin, *tri-p*-nitro- (Levene and West), A., i, 657.

Tribenzylammonium palladotribromide (Gutbier and Fellner), A., i, 542.
  palladochloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.

Tribenzylsulphinium cyanide, and its salts (Forster, Cooper, and Yarrow), T., 813; A., i, 646.

Triboluminescence (Imhof), A., ii, 229.

Tri*iso*butylammonium palladichloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 542.
  palladotrichloride (Gutbier and Fellner), A., i, 542.

Tricinnamoylphrenosin (Levene and West), A., i, 657.

Triethyl phosphite, rate of isomerisation of (v. Zawidzki and Staronka), A., ii, 83.

Triethylammonium palladichloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 542.

2:3:6-Triketo-5-benzylpiperazine (Bornwater), A., i, 121.

2:3:4-Trimethoxyacetophenone, 6-hydroxy- (Nierenstein), T., 8; A., i, 150.

3:4:6-Trimethoxyacetophenone, 2-mono- and 2:5-*di*-hydroxy- (Nierenstein), T., 7; A., i, 150.

1:2:4-Trimethoxybenzene, 5(or 6)-nitro-6(or 5)-amino- (Jones and Robinson), T., 926.

1:2:3- and 1:2:4-Trimethoxyphenanthraphenazines (Jones and Robinson), T., 928.

3:4:6-Trimethoxyphenyl 3:4-dimethoxystyryl ketone, 2-hydroxy-, and its acetyl derivative (Nierenstein), T., 8; A., i, 150.

3:4:6-Trimethoxy-2:5-quinoacetophenone (Nierenstein), T., 8; A., i, 150.

Trimethylammonium palladichloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 542.

Trimethylcotoporphyrin, *tetra*bromo-, dibromide (Fischer), A., i, 712.

1:1:4-Trimethylcoumaranone, and its semicarbazone (v. Auwers), A., i, 277.

1:1:3-Trimethyl-2:3-dihydroindolium iodide (v. Braun, Heider, and Neumann), A., i, 168.

3:7:9-Trimethyl-4:5-dihydrouric acid, 4-*mono*- and 4:5-*di*-hydroxy- (Biltz and Damm), A., i, 298.

Trimethylene. See $\alpha\gamma$-Propylene.

Trimethylene sulphide, and its derivatives (Grischkevitsch-Trochimovski), A., i, 153.

Trimethylenesulphone (Grischkevitsch-Trochimovski), A., i, 154.

1:7:9-Trimethyl-3-ethyl*spiro*-5:5-dihydantoin (Biltz and Bergius), A., i, 589.

1:3:7-Trimethyl-9-ethyluric acid, preparation and derivatives of (Biltz and Bergius), A., i, 589.

3:7:9-Trimethyl-1-ethyluric acid (Biltz and Max), A., i, 590.

Trimethyl glucose from cellulose (Denham and Woodhouse), T., 244; A., i, 320.

2:4:5-Trimethylphenylaminosulphonic acid. See ψ-Cumylaminosulphonic acid.

2:4:5-Trimethylphenylnitrosoaminosulphonic acid. See ψ-Cumylnitrosoaminosulphonic acid.

1:3:5-Trimethyl-4-piperidone, and its salts (Mannich), A., i, 635.

2:2:6-Trimethyl-4-piperidone, preparation of, and its salts (King, Mason, and Schryver), A., i, 95.

Trional, porphyrin in urine after poisoning with (Ellinger and Riesser), A., i, 715.

Trioxymethylene, condensation of dimethyl-*o*-toluidine and (v. Braun and Heider), A., i, 175.

o- and *p*-**Triphenetyltelluronium salts** (Lederer), A., i, 134.

Triphenylamines, nitro- (Piccard and Larsen), A., i, 644.

Triphenylcarbinols, action of aromatic sulphinic acids on (Hinsberg), A., i, 328.
Triphenylmethyl (Gomberg and Schoepfle), A., i, 551.
Triphenylmethylamine nitrite (Brander), A., i, 555.
  benzoyl derivative (Vosburgh), A., i, 20.
Triphenylmethylazide, *p*-chloro- (Senior), A., i, 97.
Triphenylmethylbromoamine (Vosburgh), A., i, 20.
Triphenylmethyl-*tert.*-butylamine (Brander), A., i, 555.
Triphenylmethylcarbamic acid, ethyl ester (Brander), A., i, 560.
Triphenylmethylcarbamide (Brander), A., i, 556.
Triphenylmethyl*di*chloroamine (Vosburgh), A., i, 20.
Triphenylmethylhydrazine, *p*-chloro-, hydrochloride (Senior), A., i, 97.
Triphenylmethylhydroxylamines, molecular rearrangements of (Stagner), A., i, 23.
Triphenylmethylmethylchloroamine (Vosburgh), A., i, 21.
β-Triphenylmethyl-β-methylhydroxylamines, molecular rearrangements of (Stieglitz and Stagner), A., i, 22.
Triphenylmethyloxamic acid, ethyl ester (Brander), A., i, 555.
1:2:4-Triphenyl*cyclo*pentadienedihydropyridazine, 6-nitro- (Hale), A., i, 56.
ααγ-Triphenylpropan-α-ol (Orechov and Grinberg), A., i, 451.
ααγ-Triphenyl-Δ$^{\alpha}$-propene, and bromo- (Orechov and Grinberg), A., i, 451.
Triphenylpyranol, reactions and derivatives of (Dilthey), A., i, 578.
Tripropylammonium palladichloride (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 542.
  pallado-tribromide and -trichloride (Gutbier and Fellner), A., i, 542.
Trithienylarsine (Steinkopf and Bauermeister), A., i, 303.
Tritico-nucleic acid (Read and Tottingham), A., i, 596.
Troostite, formation of (Dejean), A., ii, 477, 535.
Tropinone, synthesis of, and its dipiperonylidene derivative (Robinson), T., 762; A., i, 581.
Trouton's rule, application of, to homologous series (Herz), A., ii, 441.
Trypsin, action of pepsin on (Long and Hull), A., i, 361, 602.
Tryptic digestion. See Digestion.
Tryptophol, detection of, in fermentation products (Ehrlich), A., i, 309.
Tubera salep, colloidal solutions of (Gutbier and Kräutle), A., ii, 244, 298, 299.
Tuberculin, properties of (Rakuzin and Flier), A., i, 181.
  adsorption of, by aluminium hydroxide (Rakuzin and Flier), A., i, 428.
Tungsten, structure of (Debye), A., ii, 574.
  high-frequency spectrum of (Ledoux-Lebard and Dauvillier), A., ii, 283.
  equilibrium of water vapour with (Wöhler and Prager), A., ii, 455.
  new compounds of (Hill), A., ii, 36.
Tungsten alloys with copper, iron, nickel, and zinc (Irmann), A., ii, 478.
  Tungstates, complex, analysis of (Sweeney), A., ii, 45.
  Polytungstates, constitution of (Rosenheim, Pieck, and Pinsker), A., ii, 35.
Tungsten estimation and separation:—
  estimation of, in wolframite (Gugliamelli and Hordh), A., ii, 545.
  estimation of, in tungsten steel (van Duin), A., ii, 181.
  separation of tin and (Travers), A., ii, 545.
Tungsten steel, estimation of tungsten and silicon in (van Duin), A., ii, 181.
Turnips, swede, hydrolysis of proteins of (Williams), A., i, 375.
Turpentine, obtained in preparation of cellulose from wood (Halse and Dedichen), A., i, 398.
Tyrosinase, nature of (Folpmers), A., i, 485.
r-Tyrosine, asymmetric scission of, by bacilli (Tsudji), A., i, 679.
s-Tyrosineglycinecarbamide, and its dipotassium salt (Johnson and Hahn), A., i, 476.
Tyrosol (p-*hydroxyphenylethanol*), synthesis of, and its esters (Pischtschimuka), A., i, 87.
  detection of, in fermentation products (Ehrlich), A., i, 309.

U.

Ultramarines, constitution and formation of (Bock), A., ii, 475.
  natural and artificial (Doelter), A., ii, 147.
Unsaturated compounds, absorption spectra of (Macbeth and Stewart), T., 829; A., ii, 522.

Unsaturated compounds, state of saturation of the linking in (Ley), A., i, 261.
  molecular volumes of (Le Bas), A., ii, 442.
  condensation of (Prins), A., i, 685.
Uracil-cytosine-dinucleotide, and its brucine salt (Jones and Read), A., i, 596.
Uralite from Pellinge, Finland (Mäkinen), A., ii, 495.
Uranium salts, use of, in analysis (Thomlinson), A., ii, 41.
Uranium *di*oxide, preparation of (Parsons), A., ii, 373.
  Uranyl nitrate, explosive property of (Müller), A., ii, 373.
Uranium minerals, spectra of (Pereira-Forjaz), A., ii, 113.
Urea (*carbamide*), formation of, in the liver (Clementi), A., i, 674.
  genesis of, in tissues (Lombroso), A., i, 493.
  in muscular tissue (Hoagland and Mansfield), A., i, 674.
  formation of, by arginase (Clementi), A., i, 358.
  content of, in blood and tissues, due to a diet of oats (Lewis and Karr), A., i, 100.
  rate of excretion of (Addis and Watanabe), A., i, 367.
  excretion of, by kidneys (Addis and Watanabe), A., i, 103.
  use of alkalis in estimating (Palet), A., ii, 555.
  See also Carbamide.
Urease, action of (Falk, van Slyke, and Cullen), A., i, 182.
Urethanes, action of phosphorus pentoxide on (Bhilmann and Bjerrum), A., i, 382.
Uric acid in blood of new-born children (Kingsbury and Sedgwick), A., i, 601.
  p-nitrobenzyl ester (Lyons and Reid), A., i, 559.
  derivatives of (Biltz; Biltz and Heyn), A., i, 286.
  preparation of standard solutions of (Curtman and Freed), A., ii, 107.
  estimation of (Morris), A., ii, 279.
  estimation of, in urine (Angiolani), A., ii, 429.
  estimation of, in urine and in blood (Bogert), A., ii, 518.
ψ-Uric acid, 5-amino-, 5-chloro-, 5-hydroxy-, and their derivatives (Biltz and Heyn), A., i, 287.
Uric acid-4:5-diglycol dimethyl ether. See 4:5-Dimethoxy-4:5-dihydrouric acid.

Urine, effect of alkaline earth chlorides on the acidity of (Mayer), A., i, 239.
  excretion in, during brief fasts (Neuwirth), A., i, 366.
  human, excretion of arsenic in (Lockemann), A., i, 495.
  excretion of calcium in, and its hydrion concentration (Nelson and Williams), A., i, 103; (Nelson and Burns), A., i, 104.
  excretion of creatine in (Denis and Minot), A., i, 367.
  inhibition of enzyme action by (v. Euler and Svanberg), A., i, 676.
  excretion of magnesium in (Nelson and Burns), A., i, 104.
  sulphur compounds in (Salkowski), A., i, 304.
Urine, analytical methods relating to:—
  detection of acetoacetic acid in (Rosenbloom), A., ii, 50.
  detection of albumin in (Eicke; Edelmann), A., ii, 110; (Aufrecht), A., ii, 227.
  detection of albumin and ovalbumin in (Godfrin), A., ii, 59.
  detection of blood in (Thevenon and Rolland; Justin-Mueller), A., ii, 432.
  detection of caffeine in (Hollande and Thévenon), A., ii, 55.
  detection of cryogenine in (Grimbert), A., ii, 344; (Justin-Mueller), A., ii, 518.
  detection of indican in (Askenstedt), A., ii, 553.
  detection of indoxyl in (Palet), A., ii, 553.
  detection and estimation of indoxyl in (Justin-Mueller), A., ii, 57.
  detection of picric acid in (Yvrac), A., ii, 51.
  estimation of acetone and acetoacetic acid in (Engfeldt), A., ii, 550.
  estimation of acetone substances in (Lenk), A., ii, 399.
  estimation of albumin in (Justin-Mueller; Lenk), A., ii, 555.
  estimation of albumin and globulin in (Autenrieth), A., ii, 400.
  estimation of amino-nitrogen in (van Slyke), A., ii, 41.
  estimation of ammonia in (Folin and Bell), A., ii, 268.
  estimation of ammonia and sulphur compounds in (Weiss), A., ii, 217.
  estimation of arsenic in (Klason), A., i, 186.
  estimation of chlorine in (Heiduschka), A., ii, 38.

Urine, analytical methods relating to:—
- estimation of dextrose in (Frerichs and Mannheim), A., ii, 393; (Hiller), A., ii, 394; (Burmann), A., ii, 514.
- estimation of ethyl alcohol in (Villedieu and Hébert), A., ii, 155; (Widmark), A., ii, 547.
- estimation of β-hydroxybutyric acid in (Ohlsson), A., ii, 51; (Engfeldt), A., ii, 398.
- estimation of lactic acid in (Mayer), A., ii, 583.
- estimation of nitrogen in (Ljungdahl), A., ii, 578.
- estimation of nitrogen in, by means of potassium persulphate (Scott and Myers), A., ii, 380.
- estimation of reducing substances in (Richet and Cardot), A., ii, 556.
- estimation of selenium in (Gassmann), A., ii, 540.
- estimation of sugar in (Myers), A., ii, 221; (Cammidge), A., ii, 276; (Vanino and Bertele), A., ii, 342; (Sidersky), A., ii, 548; (Ruoss), A., ii, 549; (Lenk), A., ii, 555.
- estimation of sulphur in (Givens), A., ii, 180.
- estimation of uric acid in (Angiolani), A., ii, 429; (Bogert), A., ii, 519.
- estimation of urochromogen in (Weiss), A., ii, 431.

Urinoporphyrin, constitution of (Fischer), A., i, 713.
- after trional poisoning (Ellinger and Riesser), A., i, 715.

Urocanic acid, formation of, from histidine by bacteria (Raistrick), A., i, 499.

Urochromogen, estimation of, in urine (Weiss), A., ii, 431.

Urochromogen-reaction, method of carrying out the (Zucker and Rice), A., ii, 112.

Uroerythrin (Borrien), A., i, 577.

Urotropine. See Hexamethylenetetramine.

V.

Valency (Hinsberg), A., ii, 173, 461.
- electron conception of (Spiegel), A., ii, 28.
- in relation to crystal structure (Beckenkamp), A., ii, 296.
- relation between toxicity and (Friedsberger and Joachimoglu), A., i, 306.

Valency, subsidiary, nature of (Ephraim and Millmann), A., ii, 319; (Ephraim), A., ii, 531; (Ephraim and Wagner), A., ii, 534.

Valency volume, law of (Tutton), A., ii, 244.

*iso***Valeraldehyde**, derivatives of (Harries and Oppenheim), A., i, 211.

Valeric acid, distillation of, in steam (Richmond), A., i, 316.

Valeric acid, α-amino-, benzoyl derivative, ethyl ester (Bornwater), A., i, 137.
- $\gamma\delta$-*di*bromo-α-amino-, α-benzoyl derivative, ethyl ester (Hammarsten), A., i, 81.

Valerolactone, formation of (Taylor and Close), A., ii, 253.

Valerolactone, α-amino-δ-hydroxy-, α-benzoyl derivative and hydrochloride of (Hammarsten), A., i, 82.

Valve, Bunsen, new application of (Leighton), A., ii, 28.

Vanadium, arc spectrum of (Ludwig), A., ii, 349.
- **Vanadic acid**, reduction of, by hydrochloric acid (Edgar), A., ii, 36.
- **Polyvanadates**, constitution of (Rosenheim, Pieck, and Pinsker), A., ii, 35; (Rosenheim and Pieck), A., ii, 212.

Vanadium, estimation of, in steel (Travers), A., ii, 545.

Vanilla, extract of, estimation of vanillin in (Dox and Plaisance), A., ii, 53.

Vanillic acid, *p*-nitrobenzyl ester (Lyons and Reid), A., i, 559.

Vanillin, detection and estimation of, colorimetrically (Estes), A., ii, 343.
- estimation of, in vanilla extract (Dox and Plaisance), A., ii, 53.

Vanillophloroglucinol. See 3′-Methoxybenzophenone, 2:4:6:4′-*tetra*hydroxy-.

Vanilloresorcinol. See 3′-Methoxybenzophenone, 2:4:4′-*tri*hydroxy-.

Vanillyl *p*-nitrobenzyl ether (Reid), A., i, 333.

Vanillylidenecyanoacetic acid, ethyl ester (Lapworth and Wykes), T., 796; A., i, 572.

Vapours, condensation of (Andrén), A., ii, 192.

Vapour density, determination of (Blackman), A., [illegible].

Vapour pressure, maximum (Leduc), A., ii, 193.
- at low temperatures (Aries), A., ii, 193.
- of gels (Bachmann), A., ii, 562.
- of liquids and solids, formula for calculation of (Sch[illegible]), A., ii, 406.

Variscite from Sarrabus, Sardinia (Pelloux), A., ii, 490.
Vegetables, estimation of potassium and sodium in ashes of (Pellet), A., ii, 542.
Velocity of crystallisation in fusions (Nacken), A., ii, 363.
of metals (Czochralski), A., ii, 302.
Velocity of dissociation of compound gases (March), A., ii, 196.
Velocity of reaction, effect of pressure on (Cohen and Valeton), A., ii, 566.
influence of size of particles on (Podszus), A., ii, 300.
Velocity of solution of metals (Centnerszwer), A., ii, 135.
Veratraldehyde, bromo-, and bromonitro- (Jones and Robinson), T., 921.
Veratricsulphinide (*dimethoxysaccharin*) (Brown and Robinson), T., 952; A., i, 698.
Veratrole, 3-amino-, 5-nitro-3-amino-, *di*nitro-, *di*nitroamino-, and their derivatives (Gibson, Simonsen, and Rau), T., 75; A., i, 203.
bromonitro- and nitro-derivatives (Jones and Robinson), T., 911; A., i, 691.
5-bromo-4:6-*di*nitro- (Hindmarsh, Knight, and Robinson), T., 943.
Veratrole-4-sulphonamide, 5-nitro- (Brown and Robinson), T., 954.
Veratrole-4-sulphonic acid, 3- and 5-amino- (Brown and Robinson), T., 954.
Veratrole-4-sulphonyl chloride, and 5-nitro- (Brown and Robinson), T., 953.
Veratrylamine, 6-nitro-, and its acetyl derivative (Jones and Robinson), T., 914.
Veratryl-4:5 thiotriazoveratrole, 6-amino-, and 6-nitro- (Jones and Robinson), T., 925.
Veronal, detection of, microchemically (Tunmann), A., ii, 551.
o-**Vinylbenzyl** bromide (v. Braun), A., i, 259.
N-*o*-**Vinylbenzyldihydro*iso*indole**, and its salts (v. Braun), A., i, 170.
o-**Vinylbenzyldimethylamine**, methobromide of (v. Braun), A., i, 169.
1-*o*-Vinylbenzylpiperidine, and its salts (v. Braun), A., i, 169.
1-*o*-Vinylbenzylpyrrolidine, and its salts (v. Braun), A., i, 169.
Vinyldiacetoneamine. See 2:2:6-Trimethyl-4-piperidone.
Violanin, and its salts (Willstätter and Weil), A., i, 46.
Viola tricolor, anthocyanin from (Willstätter and Weil), A., i, 46.
Viscosity (Drucker), A., ii, 409.
absolute, measurement of (Sheppard), A., ii, 359.
and permeability (Osterhout), A., i, 135.
of liquefied gases (Verschaffelt; Verschaffelt and Nicaise), A., ii, 408.
of chlorinated aliphatic hydrocarbons (Herz), A., ii, 194.
of liquids (Kendall and Monroe), A., ii, 524, 525.
of solutions (Arrhenius), A., ii, 443.
of colloidal solutions (Arrhenius), A., ii, 130.
of solutions of metallic salts (Herz), A., ii, 361.
Vitamines, preparation of highly active (Soc. Chem. Ind. in Basle), A., i, 664.
chemical nature of (Williams), A., i, 353.
in brewers' yeast (Seidell), A., i, 362.
importance of, in diet (Osborne, Mendel, Ferry, and Wakeman), A., i, 603; (McCollum and Pitz), A., i, 604.
Vitiatine, constitution of (Johnson and Bailey), A., i, 9.
Volatile substances, apparatus for manipulation of small quantities of (Stock), A., ii, 442.
analysis of (Enklaar), A., i, 113.
Volcanoes, products of eruptions from (Brun), A., ii, 497; (di Franco), A., ii, 498.
Voltaite from Szomolnok, Hungary (Scharizer), A., ii, 490.
Voltameter, silver (Richards and Anderegg), A., ii, 14; (Bovard and Hulett), A., ii, 354.
Volumes of gases, apparatus for reduction of, to standard temperature and pressure (Fenby), A., ii, 379.
atomic, at the critical point (Le Bas), A., ii, 193.
molecular, of unsaturated compounds (Le Bas), A., ii, 442.
specific, of colloidal solutions (Kruyt), A., ii, 407.

W.

Walden inversion (Senter and Martin), T., 447; A., ii, 301.
Wassermann reaction (Walker), A., i, 527.
Water, formation of, by combination of an acid and a base (Zeitler), A., ii, 463.

Water, heat of vaporisation of (MATHEWS), A., ii, 560.
solubility of air in (COSTE), A., ii, 463.
vapour, condensation of (ANDRÉN), A., ii, 192.
cloud-like condensation of (ZWAARDEMAKER), A., ii, 63.
equilibria of, with iron and with tungsten (WÖHLER and PRAGER), A., ii, 455.
extraction of alkaloids in (LAUNOY), A., ii, 553.
Water of crystallisation, effect of light on the loss of, by salts (BEUTEL), A., ii, 63.
attachment of water in salts containing (EPHRAIM and WAGNER), A., ii, 534.
Conductivity water, preparation of (KENDALL), A., ii, 11.
NATURAL WATER :—
Potable or drinking water, sterilisation of (DAKIN and DUNHAM), A., i, 433.
action of copper sulphate on the algæ in (BADO), A., i, 107.
Rain-water, dissolved oxygen in (RICHARDS), A., i, 624.
of Sheffield, analyses of (WYNNE), A., i, 108.
Salt water, natural, analysis of (SWEENEY and WITHROW), A., ii, 423.
Sea-water, composition of, in which marine organisms are kept (McCLENDON), A., i, 105.
estimation of carbon dioxide and hydrogen-ion in (McCLENDON), A., ii, 423.
estimation of the hydrogen-ion concentration of (McCLENDON), A., ii, 266.
Spring and mineral waters, Philippine, radioactivity of (WRIGHT and HEISE), A., ii, 560.
Water analysis :—
analysis of (WINKLER), A., ii, 501.
bacteriological analysis of (CHAMOT and SHERWOOD), A., ii, 556.
analysis of, colorimetrically (LE ROY), A., ii, 418.
p-nitrophenol as an indicator in (GOLDBERG), A., ii, 498.
detection of chlorine in (LE ROY), A., ii, 98.
estimation of, in ethyl alcohol (NUSSBAUM), A., ii, 215.
estimation of, in hydrogels (FOOTE and SAXTON), A., ii, 364.
estimation of, in milk (KEISTER), A., ii, 550.
Water analysis :—
estimation of organic carbon in (BADO), A., ii, 541.
estimation of carbon dioxide in (TILLMANS and HEUBLEIN), A., ii, 332; (VAN SLYKE), A., ii, 422; (WINKLER), A., ii, 423.
estimation of hardness of (HEYN), A., ii, 218; (BEHRMAN), A., ii, 542.
estimation of hydrogen sulphide in (INCZE), A., ii, 502.
estimation of lithium and strontium in (AVERITT), A., ii, 423.
estimation of magnesium in, volumetrically (BRUCKMILLER), A., ii, 271.
estimation of nitrates in (NICHOLS), A., ii, 421.
estimation of neutrality of (MOIR), A., ii, 386.
estimation of oxygen in (BRUHNS), A., ii, 100; (NOLL), A., ii, 502.
Wax, Montan, constituents of (GRÜN and ULBRICH), A., i, 5.
Waxes, estimation of unsaponifiable matter in (WILKIE), A., ii, 429.
Weights, molecular, determination of (URBAIN), A., ii, 407.
determination of, in bromine (WRIGHT), A., ii, 28.
apparatus for determination of (v. KOZICKI and v. PILAT), A., ii, 123; (GRAEFE), A., ii, 441.
of triarylmethyls (GOMBERG and SCHOEPFLE), A., i, 551.
Wheat, action of boron compounds on the growth of (COOK and WILSON), A., i, 721.
phytic acid from bran and embryo of (BOUTWELL), A., i, 374.
effect of, on growth and development of animals (McCOLLUM, SIMMONDS, and PITZ), A., i, 184, 185.
White metal, analysis of (HOWDEN), A., ii, 580.
Wind instrument, bronze age, composition of (RATHGEN), A., ii, 316.
Wine, heavy oil of (KREMANN), A., i, 314.
Wines, reduction of the acidity of (PAUL), A., i, 246, 507, 509.
relation of acidity of, to the hydrion concentration (PAUL), A., i, 75.
formation of aldehydes in (LABORDE), A., i, 532.
turbidity of (FONZES-DIACON), A., i, 373, 374; (LABORDE), A., i, 373; (BARAGIOLA), A., i, 620.
sweet, and "mistelles," analysis of (BARAGIOLA and GODET), A., ii, 156.

(*o-Xylene, Me : Me* = 1:2 ; m-*xylene, Me : Me* = 1:3 ; p-*xylene, Me : Me* = 1:4.)

- **Wines**, microanalysis of (Ripper and Wohack), A., ii, 106, 512.
  - detection of oxalic acid in (Besson), A., ii, 516.
  - estimation of lactic acid in (Roettgen), A., ii, 583.
- **Wolframite**, estimation of tungsten in (Guglialmelli and Hordh), A., ii, 545.
- **Wood**, greenheart, constituents of (Oesterle), A., i, 505.
  - Wasabba (Baker), A., i, 682.
- **Wool fat**, constituents of (Röhmann), A., i. 78.
- **Wulfenite**, synthesis of (Dittler), A., ii, 491.

X.

- **X-rays.** See Rays, Röntgen.
- **Xanthic acid**, potassium salt, action of, on salts of halogeno-succinic acids (Holmberg), A., i, 115.
- **Xanthogallol**, constitution and derivatives of (Moore and Thomas), A., i, 460.
- **Xanthotonic acid** (Moore and Thomas), A., i, 461.
- *Xanthoxyllum*, active principles in (Bocquillon), A., i, 276.
- **Xenotime**, crystalline structure of (Vegard), A., ii, 296.
- **Xylene**, effect of, on the olfactory organ (Backman), A., i, 498.
  - separation of benzene, toluene and, from light oils (Egloff), A., ii, 338.
  - estimation of, in naphtha (Spielmann and Jones), A., ii, 339.
- *m*-**Xylene**, amino*di*hydroxy-, *di*aminohydroxy-, and *tri*amino-, and their derivatives (Herzig, Wenzel, and Kichler), A., i, 177.
- *p*-**Xylene**, additive compounds of (Pfeiffer, Jowleff, Fischer, Monti, and Milly), A., i, 207.
- *m*-**Xylenol**, thiol-, mercury salt (Friedmann), A., i, 14.
- *o*-, *m*-, and *p*-**Xylidinium** palladochlorides (Gutbier, Fellner, Kräuter, Falco, Krell, Schulz, and Woernle), A., i, 541.
- **Xylose**, preparation of (Hudson and Harding), A., i, 444.
- **4-*m*-Xylyl ethyl ketone**, 5-hydroxy- (Simonis), A., i, 580.

Y.

- **Yeast**, chemical conditions for development of reproductive organs in (Saito), A., i, 499.
  - increase in, when grown on urine containing sugar (Bokorny), A., i, 680.
  - dried, extraction of (Buchner and Skraup), A., i, 613.
  - enzymes of (Neuberg and Färber; Harden), A., i, 501.
  - proteoclastic enzymes of (Dernby), A., i, 500.
  - fermentation of dextrose by (Wilenko; v. Euler, and Haldin), A., i, 680.
  - apiculate (Kayser), A., i, 432.
  - nitrogenous nutrition of (Ehrlich), A., i, 309.
  - oxidation by (Färber), A., i, 309.
  - saccharophosphatase in (Djenab and Neuberg), A., i, 680.
  - vitamine content of (Seidell), A., i, 362.
- **Yeast-nucleic acid**, structure of (Jones and Read), A., i, 232, 233; (Levene), A., i, 670.
- **Yohimbine**, identity of quebrachine and (Filippi), A., i, 582.
- **Yttrium**, atomic weight of (Hopkins and Balke), A., ii, 34.
  - arc spectra of (Eder), A., ii, 1.
  - ferricyanide (Grant and James), A., ii, 316.
- *Yucca filamentosa*, saponin from (Chernoff, Viehoever, and Johns), A., i, 191.

Z.

- **Zeagonite** (Tiugutt), A., ii, 494.
- *Zea mais*, assimilation of organic nitrogen by (Brigham), A., i, 374.
- **Zeolites** from Leipa, Bohemia (Görgey), A., ii, 493.
- **Zinc**, extraction of (Bodenstein and Schubart), A., ii, 312.
  - velocity of solution of, in acids (Centnerszwer), A., ii, 135.
- **Zinc alloys** with copper, nickel, and tungsten (Irmann), A., ii, 479.
  - analysis of (Mossbacher), A., ii, 389.
- **Zinc** azide (Wöhler and Martin), A., i, 384.
  - chromates, and their use as pigments (Bock), A., ii, 312.
  - hydroperoxides (*perhydrates*) (Sjöström), A., ii, 533.
  - nitrite (Rây), T., 159; A., ii, 208.
  - phosphide, estimation of phosphorus in (Liberi), A., ii, 329.
  - platinichloride (Eberhard), A., ii, 313.
  - sulphate, mixed crystals of magnesium sulphate and (Viola), A., ii, 79.

Zinc sulphide, phosphorescent (MacDougall, Stewart, and Wright), T., 663; A., ii, 471.

Zinc organic compounds:—
- dimethyl, molecular heat of vapour of (Trautz), A., ii, 410.
- phenolsulphonate, estimation of, volumetrically (Adanti), A., ii, 517.

Zinc estimation and separation:—
- electroanalysis of (Guzmán Carrancio and Poch), A., ii, 509.
- estimation of (Orlik; Hastings), A., ii, 333; (Hassreidter), A., ii, 509; (Fenner and Rothschild), A., ii, 580.
- estimation of, electro-volumetrically (v. Bichowsky), A., ii, 219.
- estimation of, volumetrically (Sjöström), A., ii, 153; (Springer), A., ii, 509.
- separation of cadmium from (Ericson), A., ii, 424.

Zinc ores, occurrence of germanium in (Buchanan), A., ii, 416.

Zingerone, and its derivatives (Nomura), T., 769; A., i, 570; (Lapworth, Pearson, and Royle), T., 785; A., i, 571; (Lapworth and Wykes), T., 792; A., i, 572.

Zirconia. See Zirconium oxide.

Zirconium, atomic weight of (Venable and Bell), A., ii, 479.
- pure, preparation of (Podszus), A., ii, 373.

Zirconium alloys with nickel (Kelley and Myers), A., ii, 544.

Zirconium salts, basic, properties and constitution of (Rodd), T., 396; A., ii, 322.

Zirconium fluorides (Chauvenet), A., ii, 322.
- *di*oxide, pure, preparation of (Leuchs), A., ii, 321.
  - preparation of articles of (Ruff and Lauschke), A., ii, 95; (Podszus), A., ii, 480.
- sulphates (Chauvenet), A., ii, 322, 374.
- **Zirconyl** bromides (Chauvenet), A., ii, 221.
  - fluorides (Chauvenet), A., ii, 322.
  - hydrogen sulphate (Chauvenet), A., ii, 416.

Zirconium minerals, spectra of (Pereira-Forjaz), A., ii, 113.

Zirconyl radicle, existence of (Chauvenet), A., ii, 264.

Zymin, conditions of activation of (Harden), A., i, 501.

INDEX TO PATENTS.

British Patents, 1915.
9163, A., i, 14
11717, A., i, 91
11719, A., i, 91
14103, A., i, 56
17920, A., i, 194
18081, A., i, 197
1916.
100153, A., ii, 139
100450, A., i, 441
100452, A., i, 441
101428, A., i, 5
101636, A., i, 686
101738, A., i, 95
101973, A., i, 515
102136, A., i, 96
102216, A., i, 126
102359, A., ii, 139
102834, A., i, 197
103541, A., i, 282
103709, A., i, 332
103881, A., i, 348
104496, A., i, 599
104497, A., i, 599
104652, A., i, 410
105719, A., i, 475
105722, A., i, 475
106081, A., i, 634
107409, A., i, 664
108938, A., i, 689
French Patents.
478435, A., i, 2
479645, A., i, 15
479656, A., i, 2
479786, A., i, 15
German Patents(D. R.-P.).
285304, A., i, 721
291759, A., i, 91
293660, A., i, 41
293694, A., i, 40
293956, A., i, 50
293981, A., i, 40
294016, A., i, 53
294159, A., i, 54
294276, A., i, 359
294547, A., i, 87
294632, A., i, 359
294638, A., i, 258
294724, A., i, 377
294755, A., i, 377
294799, A., i, 271
295246, A., ii, 321
295253, A., i, 204
295337, A., i, 272
295492, A., i, 285
295624, A., i, 463
295657, A., i, 443
295736, A , i, 324
295767, A., i, 453
295817, A., i, 475
296192, A., i, 479
296501, A., i, 457
296677, A., i, 443
296796, A., ii, 467
296841, A., i, 479
296888, A., ii, 468
297243, A., i, 454
297261, A., i, 464
United States Patents.
1194465, A., ii, 87
1197462, A., i, 96
1201692, A., i, 196
1202282, A., i, 77
1203499, A., i, 96
1203500, A., i, 96
1204608, A., i, 77
1207284, A., i, 199
1207802, A., i, 127
1209163, A., i, 225
1209575, A., i, 410
1212928, A., i, 330
1213142, A., i, 331
1213261, A., i, 318
1213486, A., i, 318
1213487, A., i, 318
1215334, A., i, 377
1215335, A., i, 377
1215903, A., i, 377
1225832, A., ii, 412
1227252, A., i, 515
1227624, A., i, 582
1228926, A., i, 582
1233986, A., i, 640
1234156, A., i, 686
1235198, A., i, 664
1236570, A., ii, 530

ERRATA.

Vol. LXXXIV (Abstr., 1903).

Part I.

Page	Line	
587	7*	*for* "**87**" *read* "**37.**"

Vol. CVI (Abstr., 1914).

Page	Line	
i. 723	27	*for* "$C_{25}H_{29}O_4N_2(OMe)_3$" *read* "$C_{25}H_{29}ON_2(OMe)_3$."

Vol. CVIII (Abstr., 1915).

Page	Line	
i. 820	11*	*for* "nitrite" *read* "nitrile."

Vol. CX (Abstr., 1916).

Page	Line	
i. 135	16	*for* "**86**" *read* "**36.**"
i. 422	18	,, "SUCHARD" *read* "SUCHARDA."
i. 820	20*	,, "833" *read* "822."
i. 823	26	*delete the sentence* "Quinhydrones . . . . class" *and read* "Whilst benzoquinhydrone was found to behave differently from dyes or from *meri*quinonoid additive compounds (compare Lifschitz and Jenner, this vol., i, 45; Hantzsch, *ibid.*, 431) its absorption spectrum is by no means typical of the class, which on the contrary is optically similar to *meri*quinonoid salts."
ii. 191	5*	*for* "**Alotrichite**" *read* "**Halotrichite.**"
ii. 191	2*	,, "alotrichite" *read* "halotrichite."
ii. 192	13	,, "alotrichites" *read* "halotrichites."
ii. 335	3	,, "molten silicic acid" *read* "silica glass."
ii. 336	4	,, "thermophosphate" *read* "chromophosphate."
ii. 704	12	*insert* **Knorr**, *Angelo*, imino-esters of the thiocyanates A., i, 797.
ii. 719	11*	*for* "**Suchard**" *read* "**Sucharda.**"
ii. 741	1	,, "**Suchard**" *read* "**Sucharda.**"

Vol. CXII (Abstr., 1917)

Page	Line	
i. 227	1	*for* "6-Nitro-3:4-methylenedioxybenzoic" *read* "6-nitro-3:4-methylenedioxymandelic."
i. 249	6*	,, "SAUREZ" *read* "SUAREZ."
i. 271	17	,, "and preservation of the latter require special precautions" *read* "of the latter has not yet been accomplished."
i. 284	3	,, "quinate" *read* "quininate."
i. 340	9	,, "Bechmann" *read* "Beckmann."
i. 343	14	,, "2:4:6:3′:5′-" *read* "2:4:6:3′:4′-"
i. 343	15*	,, "*α-bromomenzyl*" read "*α-bromobenzyl.*"
i. 365	7*	,, "*photophlein*" read "*photophelein.*"
i. 366	11 12 13	,, "photophlein" *read* "photophelein."
i. 398	17	"*dl*-fenchene" *read* "*Dl*-fenchene." ,, "*d-α*-fenchene" *read* "*Dd*-fenchene."

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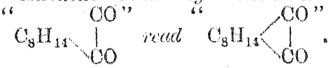
* From bottom.

Page	Line	
i. 431	13*	*for* "**Semi-barren**" *read* "**Semi-arid.**"
i. 437	13*	,, "beech" *read* "birch."
i. 466	16	,, "*Fennical*" read "*Fennicae.*"
i. 466	20*	,, "fenchene" *read* "*cyclo*fenchene."
i. 560	1*	,,  "$C_8H_{14}\diagdown\overset{CO}{\underset{CO}{\vert}}$" *read* "$C_8H_{14}\langle\overset{CO}{\underset{CO}{\vert}}$" .
i. 570	[illegible]	"*n*-hexaldehyde" *read* "*n*-heptaldehyde."

VOL. 112 (ABSTR., 1917).

Page	Line	
ii, 167	14	*for* "hydrogen" *read* "hydrogen sulphide."
ii. 324	19	,, "twinned towards the basis" *read* "twinned on the basal plane."
ii. 324	20	,, whole of line *read* "on the fractured surfaces black with metallic-adamantine lustre; in section, brown and transparent, and exhibiting."
ii. 324	22	,, "δ" *read* "ϵ."
ii. 324	23	,, "pleonast" *read* "pleonaste."
ii. 373	3*	,, "PODZUS" *read* "PODSZUS."
ii. 569	3*	,, "$\rightleftharpoons 2H_2O$" *read* "$\rightleftharpoons 2H_2O_2$."

COLLECTIVE INDEX, 1903—1912 (SUBJECTS).

Page	Col.	Line	
1833	ii	14*	*should read* "euquinine, distinction between quinine and"
2054	ii	31	*for* "1902" *read* "1908"

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* From bottom.

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

THE object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.

2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.

3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.

4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.

5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.

6. A concise statement showing the general trend of the investigation should be given at the commencement of those abstracts where the nature of the original permits of it.

7. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.

8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.

9. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

Nomenclature.

10. Employ names such as *sodium chloride*, *potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

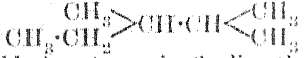
11. Term compounds of metallic radicles with the OH group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

12. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen phosphate, &c., to the acid salts. Basic salts as a rule are best designated merely by their *formulae*.

13. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO_2, carbon dioxide; P_4O_{10}, phosphoric oxide; As_4O_6, arsenious oxide; Fe_2O_3, ferric oxide.

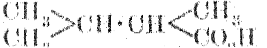
14. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter α being assigned to the first carbon atom in the formula, except in the case of CN and CO_2H, for example, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2I$ α-iodobutane, $CH_3\cdot CH_2\cdot CH_2\cdot CN$ α-cyanopropane.

15. Isomeric open chain compounds are most conveniently represented as substitution derivatives of the longest carbon chain in the formula; for example,



$$\begin{matrix}CH_3\\ CH_3\cdot CH_2\end{matrix}>CH\cdot CH<\begin{matrix}CH_3\\ CH_3\end{matrix} \text{ or } CH_3\cdot CH_2\cdot CHMe\cdot CHMe\cdot CH_3$$

should be termed βγ-dimethylpentane not methylethyl*iso*propylmethane, and



$$\begin{matrix}CH_3\\ CH_3\end{matrix}>CH\cdot CH<\begin{matrix}CH_3\\ CO_2H\end{matrix} \text{ or } CH_3\cdot CHMe\cdot CHMe\cdot CO_2H$$

should be termed αβ-dimethylbutyric acid, not αββ-trimethylpropionic, or α-methyl*iso*valeric, or methyl*iso*propylacetic acid.

16. Use names such as methane, ethane, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3\cdot[CH_2]_5\cdot CH_3$, &c. Term the hydrocarbons C_2H_4 and C_2H_2 ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-inene*. Adopt the name allene for the hydrocarbon $CH_2{:}C{:}CH_2$.

17. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH-groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, EtONa, &c., should be termed sodium methoxide, sodium ethoxide, &c.

18. The radicles indicated in the name of a compound are to be

given in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, amino-, imino-, cyano-, thiocyano-, hydroxy-, keto-.

19. Compounds analogous to the acids of the lactic series containing the OH group should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus α-ethoxypropionic acid, $\text{OEt}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, instead of ethyl-lactic acid; 3:4-diethoxybenzoic acid, $(\text{OEt})_2\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$, instead of diethylprotocatechuic acid; and α-acetoxypropionic acid, $\text{OAc}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, thus, $\text{C}_6\text{HEt}_2(\text{OH})_2\cdot\text{CO}_2\text{H}$, and not $\text{C}_6\text{H}_3(\text{OEt})_2\cdot\text{CO}_2\text{H}$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $\text{C}_6\text{HBr}_2(\text{OH})_2\cdot\text{CO}_2\text{H}$.

20. The term *ether* should be restricted to the oxides of hydrocarbon radicles and their derivatives, and the esters (so-called compound ethers or ethereal salts) should be represented by names similar to those given to metallic salts.

21. When a substituent is one of the groups NH_2, NHR, NR_2, NH or NR, its name should end in *ino*; for example, β-aminopropionic acid, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, β-anilino-acrylic acid, $\text{NHPh}\cdot\text{CH}{:}\text{CH}\cdot\text{CO}_2\text{H}$, α-iminopropionic acid, $\text{NH}{:}\text{CMe}\cdot\text{CO}_2\text{H}$.

22. Compounds of the radicle SO_3H should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

23. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteins, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

24. The Collective Index, 4th decade (1903–1912) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

Notation.

25. In empirical formulae the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

26. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

27. To economise space, it is desirable:

(a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That formulae should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^{α} for $CH_2{\cdot}CH_2{\cdot}CH_3$, Pr^{β} for $CH(CH_3)_2$, Ph for C_6H_5, Py for C_5H_4N, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$.

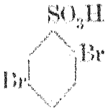
(c) That formulae should be written *in one line* whenever this can be done without obscuring their meaning.

28. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

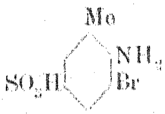
(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed; for example :—

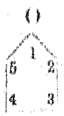


is 2 : 5-dibromobenzenesulphonic acid ;

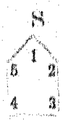


is 3-bromo-*o*-toluidine-5-sulphonic acid.

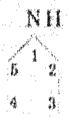
29. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulae should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (3rd edition, 1910, pp. 14—26) should be used, of which the following schemes may be regarded as typical :—



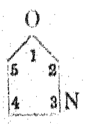
Furan.



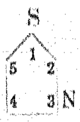
Thiophen.



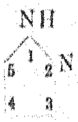
Pyrrole.



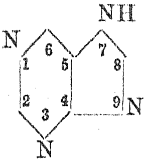
Oxazole.



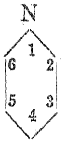
Thiazole.



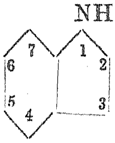
Pyrazole.



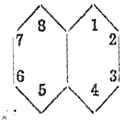
Purine.*



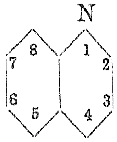
Pyridine.



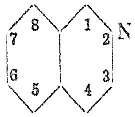
Indole.



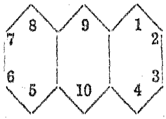
Naphthalene.



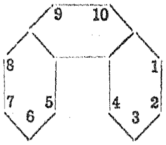
Quinoline.



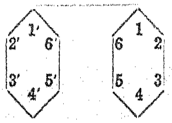
*iso*Quinoline.



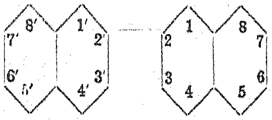
Anthracene.



Phenanthrene.



Diphenyl.



ββ-Dinaphthyl.

Manuscript.

30. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (10 × 8 in.).

31. Not more than one abstract must appear on a sheet.

32. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

33. The name of the abstractor must be written diagonally at the top left-hand corner of the first sheet of the abstract.

Proofs.

34. Abstractors are expected to read and correct proofs carefully, and to check all formulae and figures against MSS.

35. All proofs, however small, must be returned to the Sub-Editor not later than 24 hours after receipt from the printers.

⁂ The Editor's decision, in all matters connected with the Abstracts, must be considered final.

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[*] This numbering, proposed originally by E. Fischer, is adopted in the text of the *Lexikon*.

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